priate amounts of ordinary acetophenone and phenylacetylene were added as carriers, and the reaction mixtures poured into saturated NaCl and worked up as described earlier. Samples of the diluted acetophenone and phenylacetylene were recovered by preparative VPC and their specific activities determined. From the known weights of carriers added and the known specific activities before and after dilution, the yields of acetophenone and phenylacetylene were calculated. The results are summarized in Table I.

Registry No.—*cis*-1, 588-73-8; *trans*-1, 588-72-7; 3, 24343-35-9.

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(1) Supported by a grant from the National Research Council of Canada.
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Stereochemistry of Electrophilic Additions to Linear Enol Ethers

Gilbert Dana,* Odile Convert, and Caroline Perrin

Laboratoire de Chimie Organique Structurale, Université Pierre et Marie Curie, 4 Place Jussieu, 75230-Paris Cedex 05, France

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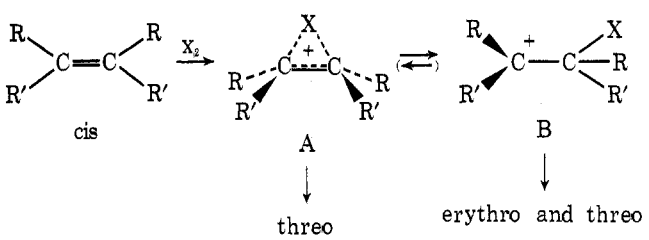
The stereospecific electrophilic anti addition of halogen to alkenes results from the existence of the bridged halonium ion A, generally more stable than the classical carbonium ion B.



Syn-addition products appear whenever the ion B is stabilized. A well-known illustration of this case is when an oxygen nonbonding electron pair stabilizes the carbocation by conjugation through the benzene ring, as in the case of anethole.[1]

The effect of an oxygen atom directly bound to the cationic carbon has been the subject of stereochemical studies in cyclic unsaturated ethers; in these cases, by adding chlorine to dihydropyrans[2] or dihydrofurans,[3] 70 and 78% of syn addition was obtained. Surprisingly, very few studies have been made on the stereochemistry of electrophilic addition to linear ethers as simple as $ROCH{=}CHCH_3$ (1, isomers *Z* and *E*).

In the present study, the results found when R = C_2H_5 (**1a**) or R = $CH_2C_6H_5$ (**1b**) are reported. In order to examine if it was possible to control the stereochemistry of the addition on this type of olefin by modifying the availability of the oxygen nonbonding electrons to the carbocation, the study of para-substituted phenol ethers (2) was simultaneously undertaken. In this case, the stabilization of the

$$p\text{-}YC_6H_4OCH{=}CHCH_3$$

2

c, Y = OMe; d, Y = Me; e, Y = H; f, Y = Cl

carbocation by oxygen electrons depends upon the nature of Y.

Experimental Section

The halogenation of ethers was carried out by adding chlorine, bromine, or iodine monochloride to a 10% solution of olefin in CCl_4 at −20° in the dark. The halogens reacted rapidly and gave the expected products, as revealed by NMR spectroscopy and chemical results. There were no by-products except in the case of ether **1a**,

$$\underset{(A)}{R\text{ (or Ar) }OCH{=}CHCH_3} \xrightarrow{X_2} \underset{(M)\ (X)}{R\text{ (or Ar) }OCHXCHX'CH_3}$$

for which, even under these experimental conditions, some products due to radical reactions appeared. The reaction of iodine addition did not proceed at low temperature and polymerization occurred at higher temperature.

The mixtures obtained were periodically analyzed by NMR spectroscopy while being maintained at −20°, thus avoiding an excess of halogen, which catalyzes the isomerization between erythro and threo dihalogenated ethers.[3]

The ratio of erythro to threo isomers depended on the configuration (*Z* or *E*) of the starting olefin (Table I). Because the product mixtures were not in the equilibrium ratio and were stable in all cases under the experimental conditions, it appeared that the reaction proceeded by kinetic control.

Table I
Stereospecificity of the Addition of Halogens to *Z* or *E* Olefins[a]

R (or Ar) OCH=CHCH₃

	Cl_2 addition, % T		Br_2 addition, % T		ICl addition, % T	
Olefin, R or Ar	*Z*	*E*	*Z*	*E*	*Z*	*E*
1a, C_2H_5	50	37	71[b]	68[b]	74	
1b, $C_6H_5CH_2$	55	40	74	65	75	
2c, *p*-$MeOC_6H_4$	58	46	83	78	90	87
2d, *p*-MeC_6H_4	60	48	92	84	98	
2e, C_6H_5	61	50	95	86	100	
2f, *p*-ClC_6H_4	62	51	100	100	100	100

[a] Percent anti addition, reproducible within 2% (threo ether from the *Z* olefin, and erythro from the *E* olefin). [b] Approximate values owing to the presence of by-products.

In the NMR spectra of the addition products, the proton H_A signal appeared as two doublets, one having a coupling constant of 2 Hz and the other one having a coupling constant of 6–8 Hz (Table II). It was noticed, as in other well-known cases,[4] that the isomer having the smallest J_{AM} value appeared at a lower field.

These data allowed us to classify the isomers in two well-characterized families: in the present study, the isomer having the smallest coupling constant (lower field signal) is the threo isomer (vide infra).

Discussion

The assignment of the erythro or threo configuration to each of the two spectroscopic families is based on the two following criteria.

(a) The anti addition becomes more or less stereospecific depending on the nature of the electrophilic reagent: $I^+ > Br^+ > Cl^+$ (Table I).

Table II
NMR Spectra of Erythro and Threo Dihalogenated Ethers[c]

R (or Ar) OCHXCHX′CH$_3$
(A) (M) (X)

R or Ar	X	X′	δ H$_A$, ppm (J_{AM}, Hz) Erythro[d]	δ H$_A$, ppm (J_{AM}, Hz) Threo[e]	δ H$_X$, ppm[a] Erythro	δ H$_X$, ppm[a] Threo	δ H$_M$, ppm[b]
C_2H_5	Cl	Cl	5.5 (5.8)	5.7 (2.8)	1.63	1.63	
	Br	Br	5.86 (7.8)	6.20 (2)	1.85	1.85	
	Cl	I	5.5 (7.6)	5.9 (2)	2.03	1.97	4.35
$C_6H_5CH_2$	Cl	Cl	5.45 (5.8)	5.63 (2.4)	1.59	1.63	4.17
	Br	Br	6.01 (7.6)	6.12 (2)	1.84	1.88	4.38
	Cl	I	5.42 (7.6)	5.8 (2)	1.97	1.97	4.44
p-$MeOC_6H_4$	Cl	Cl	5.87 (6.2)	6.00 (2.4)	1.72	1.76	4.33
	Br	Br	6.13 (8)	6.45 (2)	1.97	2.03	4.55
	Cl	I	5.85 (8)	6.17 (2)	2.07	2.07	4.50
p-MeC_6H_4	Cl	Cl	5.90 (6.2)	6.05 (2.4)	1.70	1.75	4.33
	Br	Br	6.12 (8)	6.43 (2)	1.95	2.02	4.55
C_6H_5	Cl	Cl	5.97 (6.2)	6.08 (2.4)	1.67	1.73	4.33
	Br	Br	6.20 (8)	6.50 (2)	1.98	2.02	4.55
	Cl	I		6.30 (2)		2.10	4.50
p-ClC_6H_4	Cl	Cl	5.91 (6.2)	6.07 (2.4)	1.72	1.76	4.33
	Br	Br	6.21 (8)	6.50 (2)	1.97	2.02	4.55
	Cl	I	5.90 (8)	6.20 (2)	2.08	2.08	4.50

[a] Doublet (J_{MX} = 7 Hz). [b] Signals of the two isomers together. [c] Chemical shifts were expressed relative to tetramethylsilane used as internal reference for a 10% solution of dihalogenated products in CCl_4. [d] Registry no. are, respectively, 54912-01-5, 54912-03-7, 54912-05-9, 54912-07-1, 54912-09-3, 54934-05-3, 54912-12-8, 54912-14-0, 54912-16-2, 54912-18-4, 54912-20-8, 54912-22-0, 54912-24-2, 54934-06-4, 54912-28-6, 54934-07-5. [e] Registry no. are, respectively, 54912-02-6, 54912-04-8, 54912-06-0, 54912-08-2, 54912-10-6, 54912-11-7, 54912-13-9, 54912-15-1, 54912-17-3, 54912-19-5, 54912-21-9, 54912-23-1, 54912-25-3, 54912-26-4, 54912-27-5, 54912-29-7, 54912-30-0.

Table III[a]
NMR Spectroscopy of Enol Ethers. Chemical Shift of ^{13}C in the Propenyl Group

R (or Ar) OCH=CHCH$_3$
(α) (β)

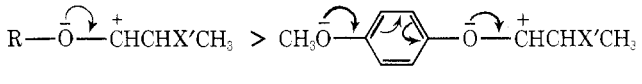
	1a R = C_2H_5		1b R = $CH_2C_6H_5$		2c Y = OMe		2d Y = CH_3		2e Y = H		2f Y = Cl	
	Z	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*
δC$_\alpha$	145.23	146.27	145.0	146.12	141.81	143.23	141.19	142.25	140.69	141.83	140.38	141.68
δC$_\beta$	100.84	98.41	101.73	99.29	105.95	106.68	106.48	107.32	107.18	108.08	108.07	109.01
δCH$_3$	9.22	12.59	9.32	12.58	9.32	12.18	9.35	12.25	9.34	12.23	9.37	12.13

[a] ^{13}C NMR spectra were determined using a Varian XL-100-12 NMR spectrometer, operating at 25.20 MHz in pulsed Fourier transform mode with proton noise decoupling (precision ±0.04 ppm). Chemical shifts are expressed in parts per million relative to tetramethylsilane used as internal reference for $CDCl_3$ solutions (0.4–0.5 *M*).

(b) By changing the substituent Y in olefins **2**, the availability of the oxygen electrons toward the carbocation decreases in the order *p*-MeO > *p*-Me > H > *p*-Cl. For any given halogen and a series of olefins **2** with configuration *Z* or *E* stated, the stereospecificity of the anti addition must increase from Y = *p*-MeO to Y = Cl (Table I).

Those two criteria coincide when the erythro structure is attributed to dihalogenated ethers having a coupling constant J_{AM} = 6.4–8 Hz and the threo structure is attributed to the ones having a coupling constant J_{AM} = 2–2.4 Hz.

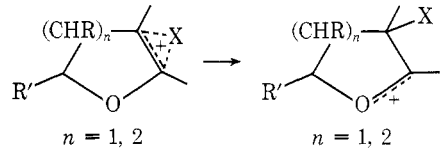
It is noteworthy that with olefins **2**, even when Y = MeO, the anti addition always remains more stereospecific than for the olefins **1** in spite of the resonance hybrid which greatly favors the opening of the bridged ion A.



In all cases, the nonbonding electrons of a phenol ether **2** remain less available than those of an alcohol ether **1**.

On the other hand, the observed results for the *Z* or *E* olefins show that the *Z* isomer systematically yields more anti addition than the *E* isomer (the contrary is usually noticed with simple olefins[5]). That result means that an attractive effect exists between OR and CH_3 in the bridged cis ion A, as has been already noticed in the original enol ethers.[6] The bridged trans ion A is less stable than its cis isomer and is more prone to open.

It is interesting to compare these results with those obtained with cyclic ethers[2,3] (which may be classified as alcohol ether 1 of *Z* configuration). The higher yields observed in syn addition indicate in fact that the corresponding bicyclic halonium ions are even less stable than in the linear series.



n = 1, 2 *n* = 1, 2

The study of the spectroscopic properties of the olefins **2** shows that a good correlation exists between the chemical shift $\delta\ ^{13}C_\beta$ in NMR spectroscopy (Table III) and the Hammett constants σ (Y): $\delta\ ^{13}C_\beta = 107.18 + 0.436\sigma$ (Y) for the *Z* olefins ($|\delta_{calcd} - \delta_{obsd}| \leq 0.08$ ppm); $\delta\ ^{13}C_\beta = 108.08 + 0.436\sigma$ (Y) for the *E* olefins ($|\delta_{calcd} - \delta_{obsd}| \leq 0.15$ ppm). It is well known that in unsaturated systems, the contribution of the π electron density is an important component in the ^{13}C chemical shift, especially for analogous ring-substituted phenyl vinyl ethers.[7] Therefore the chemical shift of C_β seems to be a good criterion to evaluate the availability of the oxygen nonbonding electrons toward the benzene ring, whatever be the series.

In Figure 1, the percent of anti addition found when adding chlorine, bromine, and iodine monochloride is reported against the chemical shift of C_β. A rough linear relationship is found for chlorine: it appears that the same phenomenon occurs with the alcohol ether or the phenol ether, the six points falling on the same empirically derived straight line.

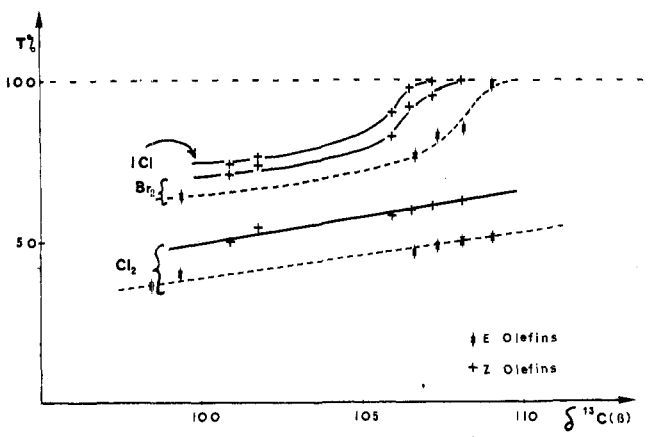


Figure 1. Correlation between the selectivity of electrophilic anti addition and the availability of π electron on C_β (evaluated by means of its chemical shift, see Hammett correlation in text).

When adding bromine or iodine monochloride, different curves tending towards the asymptotic value of 100% anti addition for electron-withdrawing groups are observed. In these cases, there is a stabilization of A due to the electrophilic reagent and a destabilization of B due to the electron-withdrawing groups. Since the concentration of B (at equilibrium) is an exponential function of $-\Delta G/RT$, its contribution to the reaction becomes negligible. In fact, the equilibrium conditions are not attained, as the *Z* and *E* isomeric enol ethers do not give the same erythro:threo ratio.

In conclusion, the electrophilic addition simultaneously involves the two intermediate species A and B, the bridged halonium ion and the classical carbonium ion.

Registry No.—(*Z*)-**1a**, 4696-25-7; (*E*)-**1a**, 4696-26-8; (*Z*)-**1b**, 32426-80-5; (*E*)-**1b**, 32426-79-2; (*Z*)-**2c**, 51896-37-8; (*E*)-**2c**, 51896-38-9; (*Z*)-**2d**, 51896-41-4; (*E*)-**2d**, 51896-42-5; (*Z*)-**2e**, 4696-23-5; (*E*)-**2e**, 4696-24-6; (*Z*)-**2f**, 51896-45-8; (*E*)-**2f**, 54912-31-1; Cl_2, 7782-50-5; Br_2, 7726-95-6; ClI, 7790-99-0.

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1-Phenylpiperidine-2,4,6-trione

John D. Mee

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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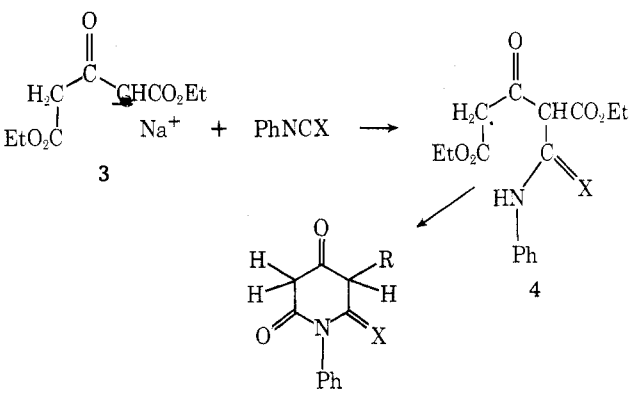
The synthesis of the title compound has been the subject of several papers that have appeared in the chemical literature. The compound identified by Kaushal[1] as **5c** was subsequently shown[2] to be an adduct of aniline and zinc chloride. Later, Nakhre and Deshapande[3] reported that **5c** may be obtained by the reaction of 3-oxoglutaric anhydride with aniline in anhydrous ether. Repetition of this reaction yielded the anilic acid **1**, which readily lost carbon dioxide upon heating, with the formation of acetoacetanilide (**2**).

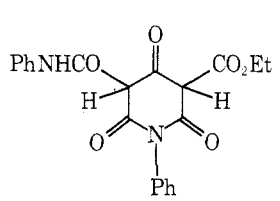
$$\underset{\mathbf{1}}{PhNHCOCH_2COCH_2CO_2H} \xrightarrow{-CO_2} \underset{\mathbf{2}}{PhNHCOCH_2COCH_3}$$

More recently, Junek, Metallidis, and Ziegler[4] described the reaction of the sodium salt of diethyl 3-oxoglutarate (**3**) with phenyl isothiocyanate[5] to give the ester **5a** via the intermediate formation of **4**.



5a, R = CO_2Et; X = S
b, R = CO_2Et; X = O
c, R = H; X = O

When the reaction was conducted using phenyl isocyanate, it was reported[4] that the product was not the expected ester **5b**, but **5c**, in which an ethoxycarbonyl group had been lost. We have re-examined this reaction, but have been unable to find any trace of **5c** among the products. The ester **5b** was obtained, accompanied by a small amount of a compound formed by reaction of **5b** with a second molecule of phenyl isocyanate, for which **6** is a probable structure.



6

Finally, we have been able to synthesize the required trione **5c** by acidic hydrolysis of **7**, which is obtained by reaction of diethyl 3-oxoglutarate with aniline.[6]

The NMR spectrum of **5c** in DMSO-d_6 indicates three types of exchangeable protons, with singlets at δ 3.65 (2 H), 5.42 (1 H), and 17.1 (1 H, broad). Such a spectrum is consistent only with one of the two possible monoenol tautomers, **8** or **9**.