JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 2, 26–34 (1989)

RELATIVE RATES OF BROMINATION AND CHLORINATION OF 4-SUBSTITUTED CYCLOPENTENES IN METHANOL, ETHANOL AND ACETIC ACID

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ABSTRACT

A set of 4-monosubstituted cyclopentenes, $\overline{CH{=}CHCH_2CHXCH_2}$, were synthesized and their relative rates (k_X/k_H) for bromination and chlorination were determined in methanol, ethanol and acetic acid at 25 °C by competitive method. $\log(k_X/k_H)$ for most of the substituents can be correlated by means of Taft's equation, $\log(k_X/k_H) = \rho_I \sigma_I + C$. In methanol $\rho_{I,Br_2} = -2{\cdot}91$, $\rho_{I,Cl_2} = -0{\cdot}49$, in ethanol $\rho_{I,Br_2} = -3{\cdot}07$, $\rho_{I,Cl_2} = -0{\cdot}70$ and in acetic acid $\rho_{I,Br_2} = -1{\cdot}64$, $\rho_{I,Cl_2} = -0{\cdot}65$. The presence of $C(<0)$ is due to a constant steric effect. The deviation of X = H is ascribed to the absence of the steric effect and that of X = CO_2Me and CO_2Et is accounted for in terms of anchimeric assistance. For chlorination no anchimeric assistance was observed.

Substituent effects on electrophilic additions of halogens to olefinic compounds have been studied by many workers.[1] In the reported works the systematically studied aliphatic substrates were all unsymmetrical and acyclic alkenes. The halogenation in polar hydroxylic solvents follows the Ad_ECl mechanism,[2] which involves an ionic intermediate that may vary from a halogen-bridged halonium to an open carbocation (halonium–carbocation spectrum) depending upon the substituents attached to the two unsaturated carbon atoms.[3] A 4-substituted cyclopentene molecule possesses a plane of symmetry passing through carbon 4 and the centre of the double bond. This cyclic alkene reacts via a bridged halonium intermediate in halogenation.[4] Considering the structural feature of the substrate, one might expect the halonium intermediate or related transition state to be symmetric, i.e. that the halogen would bridge the two double-bond carbon atoms equally, if there were no other specific interactions. It will be interesting to study the structural effects on the reactivity of halogenations of this series of compounds. We synthesized a set of 4-substituted cyclopentenes and determined their relative rates of bromination and chlorination in methanol, ethanol and acetic acid at 25 °C.

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0894–3230/89/010026–09$05.00

Received 12 January 1988
Revised 4 April 1988

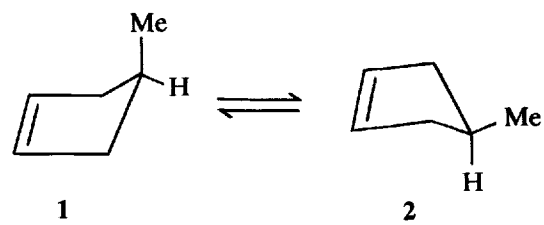
Table 1. Relative rate constants for bromination and chlorination of $\overline{CH{=}CHCH_2CHXCH_2}$ in methanol, ethanol and acetic acid at 25 °C

Substituent(X)		H	Me	OH	OMe	CO_2Me	CO_2Et	OAc	Br	Cl	CN
	MeOH	1·00	0·80 ±0·05	0·15 ±0·01	0·16 ±0·01	0·16 ±0·01			0·030 ±0·004	0·023 ±0·002	0·017 ±0·001
k_X/k_H of bromination	EtOH	1·00	0·68 ±0·01	0·12 ±0·02	0·12 ±0·01		0·10 ±0·01		0·022 ±0·003	0·020 ±0·004	0·010 ±0·002
	AcOH	1·00	0·84 ±0·02		0·25 ±0·01	0·72 ±0·03	0·48 ±0·05	0·19 ±0·01	0·13 ±0·01	0·15 ±0·01	0·07 ±0·01
	MeOH	1·00	0·95 ±0·05	0·59 ±0·04	0·58 ±0·03	0·64 ±0·04			0·51 ±0·04	0·51 ±0·04	0·46 ±0·04
k_X/k_H of chlorination	EtOH	1·00	0·85 ±0·03	0·60 ±0·03	0·58 ±0·05		0·58 ±0·04	0·50 ±0·03	0·39 ±0·02	0·39 ±0·03	0·32 ±0·02
	AcOH	1·00	0·93 ±0·06		0·61 ±0·06	0·58 ±0·04		0·49 ±0·03	0·49 ±0·03	0·47 ±0·04	0·35 ±0·05

RESULTS AND DISCUSSION

The results of relative rate measurements are summarized in Table 1. In both bromination and chlorination in all three solvents $k_{Me}/k_H < 1$ (≈0·7–0·9) is always observed. Thus it can be concluded that the reactions are decelerated by the methyl group. Although methyl connected to a sp^3 carbon atom may behave as an electron-withdrawing group in some cases,[5] in halogenations of alkenes methyl attached to a saturated carbon atom appears to be electron-releasing. In the bromination of linear alkenes in methanol and acetic acid, introduction of a methyl to an α-carbon of the double bond always leads to an acceleration of the reaction so long as its steric effect is negligible.[6] It cannot be expected that a methyl group is electron-releasing when it is connected to a sp^3 carbon atom on an open chain and becomes electron-withdrawing when the carbon atom is on a ring. Based upon these considerations we concluded that the methyl group of 4-methylcyclopentene is electron-releasing in the reaction, in accord with its σ_I (<0).

The observed deceleration by the methyl should be accounted for in terms of steric effect. In *syn* or *anti* addition to a cyclic olefinic compound, generally it is more difficult for the reagent to attack the more hindered side.[7] For example, epoxidation of 4-methylcyclopentene gave 76% addition from the less hindered side and 24% from the more hindered side.[8] It should be so in halogenation too. Thus the 4-methyl deactivates the reactions through steric effects. So long as the steric effect of the methyl is not cancelled by its electronic effect, the relative rate $k_{Me}/k_H < 1$. Nevertheless, it should be noted that the steric effect of the 4-methyl group is small, because (1) the methyl is not a very hindering group and is situated in a remote position to the reaction seat; (2) only one side of the cyclopentene ring can be hindered by the 4-methyl while the other side is free of this interaction; (3) the steric effect is considerable only when the substituent is in an axial position (conformation 1):



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For the same reasons the steric effects of other substituents in the series cannot be large and should not vary in a detectable way.

The data obtained in bromination were correlated with the inductive substituent constants (σ_I).[9] The results illustrated in Figure 1 show that in all the solvents the points of X = H, CO_2Me or CO_2Et always lie above the line correlating all the other substituents:

$$\text{MeOH} \quad \log(k_X/k_H) = -2{\cdot}91\ \sigma_I - 0{\cdot}17 \quad (|r| = 0{\cdot}992) \tag{1}$$

$$\text{EtOH} \quad \log(k_X/k_H) = -3{\cdot}07\ \sigma_I - 0{\cdot}24 \quad (|r| = 0{\cdot}994) \tag{2}$$

$$\text{AcOH} \quad \log(k_X/k_H) = -1{\cdot}64\ \sigma_I - 0{\cdot}15 \quad (|r| = 0{\cdot}980) \tag{3}$$

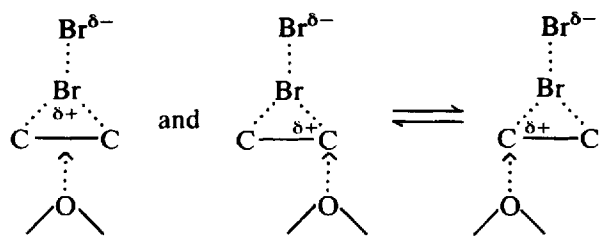
As discussed above, the positive deviation of X = H is due to the absence of steric effect of the 4-substituent which exists for the other substituents on the line. As this steric effect is practically constant (it is so for linear alkenes too[10]) throughout the series, the substituents can satisfy a linear correlation except some points provided by the substituents that may interact specifically with the reaction seat. According to Taft's equation:[11]

$$\log(k_X/k_H) = \text{general inductive} + \text{steric} + \text{resonance effects} \tag{4}$$

In the series of 4-substituted cyclopentenes, the resonance effects can be omitted and the inductive effect (including field effect) is expressed in terms of $\rho_I\ \sigma_I$. Thus the intercepts of equations (1)–(3) should be considered as steric effects of the series. Apparently the absolute values of the intercepts are all small ($\approx 0{\cdot}2$).

The deviation of X = CO_2Me and CO_2Et can be plausibly ascribed to the anchimeric assistance of carbomethoxyl and carboethoxyl groups. Since the double bond in 2-(Δ^3-cyclopentenyl)ethyl tosylate and *p*-nitrobenzenesulfonate can participate directly in the solvolysis of these esters,[12] it is not surprising to observe the neighbouring group effect of the 4-alkoxyl when the double bond is the reaction seat. Moreover, anchimeric assistance in electrophilic additions has also been found in addition of 2,4-dinitrobenzenesulphenyl chloride to 3,4-dicarbomethoxylcyclohexene[13] and in bromination of γ,δ-unsaturated esters.[14] From Figure 1 it can be seen that the neighbouring group effect is more important in the less nucleophilic solvent (AcOH) and is more effective for the more mobile carbomethoxyl group. Nevertheless, as shown by the results in another study[6a] and in this work, the transition state stabilization provided by nucleophilic assistance is small since a considerable amount of charge is delocalized on the halogen in a halonium. The interaction between halogen and double bond is related to charge-transfer complex formation while the nucleophilic assistance should be feeble electrostatic interaction.

We had expected a symmetrical halonium-like transition state for the cyclopentene derivatives. In the presence of nucleophilic participation or solvation, can the assumed symmetry be maintained? That is, which of the following transition states should be more possible?



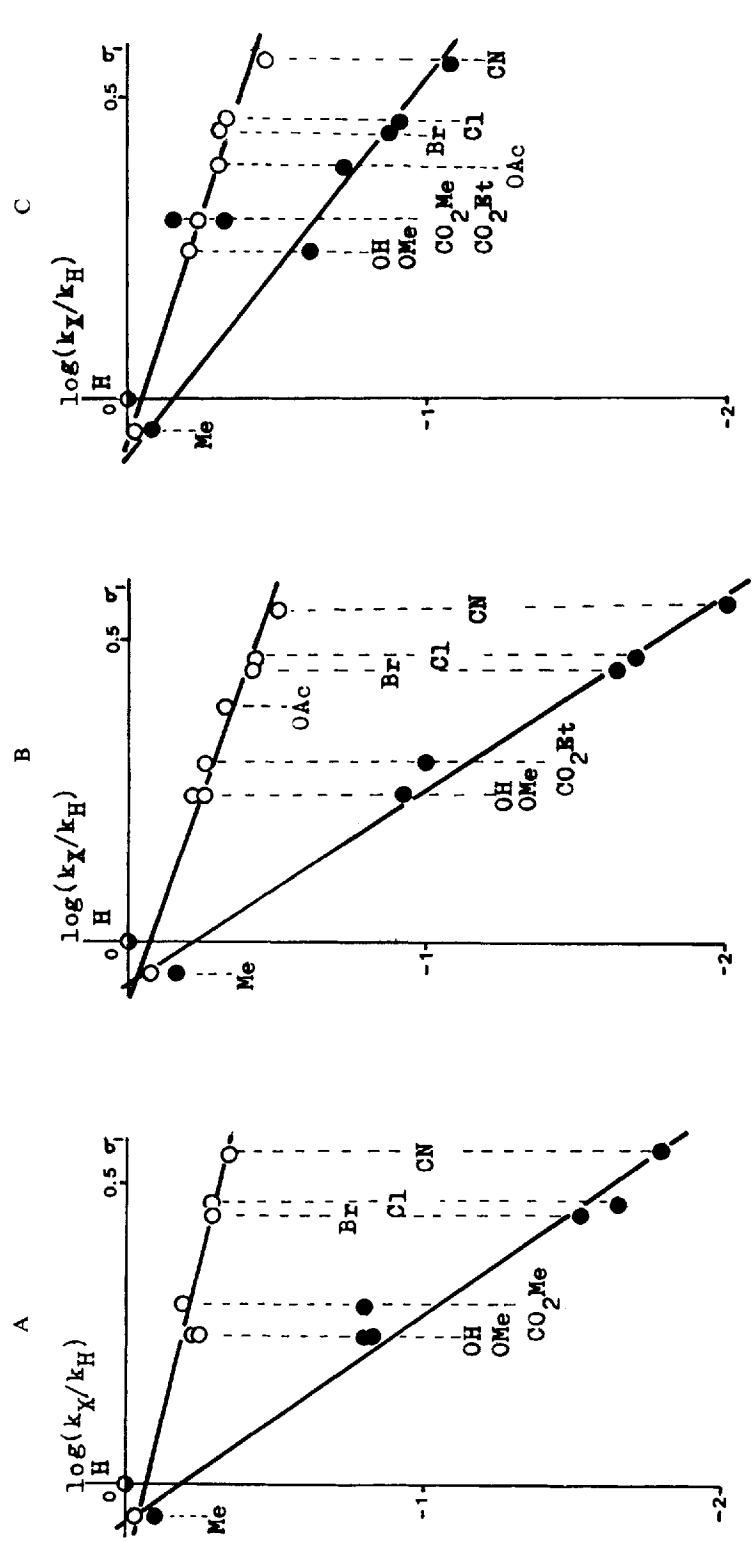


Figure 1. Plots of $\log(k_X/k_H)$ vs. σ_I for bromination (●) and for chlorination (○) of $\overline{CH{=}CHCH_2CHXCH_2}$ in methanol (A), ethanol (B) and acetic acid (C)

It seems more reasonable to assume an unsymmetric transition state since (1) the bridging ability of the nucleophilic oxygen of the solvent or of the neighbouring group is lower than that of the halogen and its interaction with one of the two carbon atoms will influence the symmetry of the system; (2) an unsymmetrical transition state is entropically more favourable; and (3) this is consistent with an Ad_ECl intermediate mechanism.[6a,15] Nevertheless, we still believe that the assisted halonium of a symmetrical substrate is more symmetrical than that of an unsymmetrical substrate as the nucleophilic assistance is rather feeble.

For bromination in the two more nucleophilic solvents (MeOH and EtOH) $\rho_I \approx -3$ whereas in AcOH $\rho_I = -1{\cdot}64$. Comparing with $\rho_I = -6{\cdot}7$ for the series $RCH_2CH{=}CH_2$[16] and $\rho_I = -5{\cdot}4$ for the series $RCH_2CH{=}CHPh$[6b,17] in bromination in methanol, the influence of the substituents in the series of $\overbrace{CH{=}CHCH_2CHXCH_2}$ is considerably reduced. As an olefin is more reactive in a solvent of higher ionization power (Y),[2a] the variation of ρ_I with Y of the solvents does not follow the reactivity–selectivity principle. As in the case of linear alkene bromination for which ρ^* is constant in different solvents,[2a,6a,18] this observation can be accounted for neither by the position of transition state nor by the degree of charge delocalization in the transition state of the rate-controlling step although these factors can all be influenced by solvent. In bromination via the Ad_ECl mechanism, the apparent rate constant $k_{app} = Kk_{rcs}$ where K is the formation constant of the charge-transfer complex and k_{rcs} is the rate constant of the rate-controlling step. As long as both $\log K$ and $\log k_{rcs}$ can be correlated linearly with σ_I, $\rho_{I,app} = \rho_{I,K} + \rho_{I,k_{rcs}}$. If the effect of solvent on $\rho_{I,K}$ and on $\rho_{I,k_{rcs}}$ could be studied separately, it would help in understanding these 'anomalous' effects of solvent on ρ_{app}.

The results of correlation analysis for the data of chlorination are shown in Figure 1. In the solvents all substrates can be correlated linearly with σ_I except X = H:

$$\text{MeOH} \quad \log(k_X/k_H) = -0{\cdot}49\,\sigma_I - 0{\cdot}07 \quad (|r| = 0{\cdot}960) \tag{5}$$

$$\text{EtOH} \quad \log(k_X/k_H) = -0{\cdot}70\,\sigma_I - 0{\cdot}07 \quad (|r| = 0{\cdot}973) \tag{6}$$

$$\text{AcOH} \quad \log(k_X/k_H) = -0{\cdot}65\,\sigma_I - 0{\cdot}05 \quad (|r| = 0{\cdot}981) \tag{7}$$

Similar to the discussion for bromination, the intercepts of the equations are related to steric effects. The absolute values (0·05–0·07) of these intercepts are smaller than those in bromination. This observation might imply smaller steric effects or could be due to less sensitivity to structural effects in chlorination than in bromination.

In contrast to bromination, in all the solvents the points provided by X = CO_2Me and CO_2Et don't deviate from the line of correlation. This implies that anchimeric assistance did not take place in chlorination. In their study on halogenation of $CH{=}CH(CH_2)_3OH$ Williams *et al.*[17] found that the importance of the neighbouring group effect varies with the electrophile. For iodination the effect is considerable while for chlorination it can hardly be detectable. This is in accord with the reactivity–selectivity principle. The chlorine, which is a more reactive electrophile than the bromine, reacts so fast with the olefin that the olefin molecule has no time to reach the conformation the anchimeric assistance needs. $|\rho_I|$ values for chlorination are generally smaller than those for bromination. This is also in harmony with the reactivity–selectivity principle and implies that in chlorination the major contribution to ρ_I is from $\rho_{I,k_{rcs}}$. Since chlorination is faster than bromination, an earlier transition state which corresponds to a smaller $|\rho_I|$ is expected according to the Hammond postulate.[19] Bienvenue-Goetz *et al.*[20] compared the polar reaction constant ρ^* for bromination and for chlorination of alkenes $CH_2{=}CHCH_2X$ and found that $|\rho^*_{Cl_2}|(= 2{\cdot}9)$ is only slightly less than $|\rho^*_{Br_2}|(= 3{\cdot}1)$ despite the large reactivity difference between the two halogens. This result was

explained in terms of the less efficient charge delocalization ability of the chlorine atom which is a poor neighbouring group. The difference in selectivity change between the two series $CH_2{=}CHCH_2X$ and $\overline{CH{=}CHCH_2CHXCH_2}$ can plausibly be ascribed to their different transition state structures of the rate-controlling step. The transition state for chlorination of the unsymmetrical linear alkenes should be less symmetric and possess more carbocation character than that of the symmetrical cycloalkenes which should be more symmetric and possess more chloronium character, even when the feeble nucleophilic solvation is taken into consideration. The latter corresponds to a smaller $|\rho_{I,k_{res}}|$ than the former.

Although the difference in ρ_I is small, it appears that $|\rho_I|$ decreases as the ionization power of the solvent increases. This might support the assumption that $\rho_{I,k_{res}}$ contributes considerably to ρ_I. The rate-controlling step involves ionization of the charge-transfer complex and is promoted by solvents of high ionization power. If the reactivity–selectivity principle is applied, the susceptibility to the influence of substituents on the reactivity should decrease as the polarity of solvent increases.

EXPERIMENTAL

Physical measurements

IR measurements were made with a Pye Unicam SP3-300 spectrometer. ^{1}H-NMR spectra were recorded on a Joel PMX-60 spectrometer. Chemical shifts are in ppm (δ) downfield from TMS. MS analyses were carried out on a VG 7070E-HF mass spectrometer.

Materials

Cyclohexene and cyclopentene were purchased from Fluka. The following compounds were synthesized by literature procedures: 4-hydroxycyclopentene,[21] 4-chlorocyclopentene,[22] 4-cyanocyclopentene,[23] 4-methoxycyclopentene,[24] Δ^3-cyclopentenecarboxylic acid,[23] 4-bromocyclopentene,[25] and Δ^3-cyclopentenyl acetate.[25]

4-methylcyclopentene. Lithium dimethylcuprate[26] prepared from a solution (80 ml) of methyl lithium (0·7 M) in diethyl ether and cuprous iodide (11·2 g) was cooled to −50 °C. A solution of Δ^3-cyclopentenyl *p*-toluenesulfonate[23] (16 g) in 100 ml of diethyl ether was dropped to the cooled etheral solution of lithium dimethyl cuprate. The mixture was stirred at −30 °C for 12 hr. The reaction mixture then was hydrolysed with saturated ammonium chloride solution. The organic layer was washed twice with saturated sodium chloride solution, then dried ($MgSO_4$). The solvent was removed and the residue was distilled to yield 4 g of crude product. 68% yield. b.p. 60–64 °C (lit. 62 °C). Further purification was carried out on a preparative g.l.c. *m/z* 82(M^+, 28%), 67(100).

Ethyl Δ^3-cyclopentenecarboxylate. A mixture of anhydrous ethanol (8 ml), chloroform (10 ml), sulfuric acid (1 ml) and Δ^3-cyclopentenecarboxylic acid (1·5 g) was refluxed for 3 hr. Then after removal of most ethanol–chloroform by distillation, the residue was mixed with water and extracted with diethyl ether. The extract was washed with 5% aqueous sodium carbonate solution and water, and dried ($MgSO_4$). Ether was removed by distillation and the

residue was purified by chromatography on a column of SiO_2, using light petroleum (b.p. 30–60 °C)–acetone (6:1), to yield 1·4 g of yellow oil. 75% yield. *m/z* 140(M^+, 21%), 111(8), 95(18), 67(100).

Methyl Δ^3-cyclopentenecarboxylate was prepared by the same procedure as the preparation of ethyl Δ^3-cyclopentenecarboxylate except that methanol was used in place of ethanol. 1·2 g of light yellow oil was obtained. 70% yield. *m/z* 126(M^+, 21%), 111(12), 94(42), 67(100).

IR and NMR spectral data of these compounds are listed in Table 2.

Relative rate measurements

All solvents had been treated by standard procedures before use. Two olefins and an internal standard were dissolved in the solvents to prepare stock solutions (in methanol and ethanol the concentration of each olefin is 0·01 M while in acetic acid it is 0·02 M). In each run 2 ml of stock solution was introduced into a thermostatted water-jacketted dark reactor equipped with magnetic agitator. For bromination the solution of bromine (0.5 M) placed in a constant-temperature bath was added via a syringe and for chlorination chlorine gas was bubbled through the solution. In all experiments the consumption of the more reactive substrate was never more than 2/3. In chlorination the addition of a radical scavenger did not influence the results, so the scavenger was not used. G.l.c. analysis was carried out on a

Table 2. IR and NMR data of $\overbrace{CH{=}CHCH_2CHXCH_2}$

Substituent (X)	IR. ν_{max} cm^{-1}	NMR
OH	3340, 3070, 1620, 950, 840	$\delta_H(CDCl_3)$ 5·7(s, 2H, =CH × 2), 4·5 (heptet, 1H, CH), 3·5(s, 1H, OH) 2·0–2·9(m, 4H, CH_2 × 2)
Br	3065, 2880, 1610, 910, 678	$\delta_H(CCl_4)$ 5·8(s, 2H, =CH × 2), 4·5 (m, 1H, CH), 2·6–3·2(m, 4H, CH_2 × 2)
Cl	3080, 2900, 1610, 690	$\delta_H(CCl_4)$ 5·8(s, 2H, =CH × 2), 4·5 (m, 1H, CH), 2·3–3·2(m, 4H, CH_2 × 2)
CN	3080, 2870, 2250, 1620, 670	$\delta_H(CCl_4)$ 5·7(s, 2H, =CH × 2), 2·7–3·3(m, 5H, CH_2 × 2, CH)
Me	3080, 2840, 1620, 1360	$\delta_H(CCl_4)$ 5·7(s, 2H, =CH × 2), 1·7–2·8(m, 5H, CH_2 × 2, CH), 1·0(d, 3H, CH_3)
OAc	3080, 2860, 1740, 1620, 1250	$\delta_H(CCl_4)$ 5·8(s, 2H, =CH × 2), 5·3 (heptet, 1H, CH), 2·1–3·1(m, 4H, CH_2 × 2), 2·0(s, 3H, CH_3)
OMe	3060, 2820, 1620, 960	$\delta_H(CCl_4)$ 5·7(s, 2H, =CH × 2), 4·1 (m, 1H, CH), 3·3(s, 3H, OCH_3), 2·0–2·8(m, 4H, CH_2 × 2)
CO_2H	3080, 1700, 1620, 1240, 940	$\delta_H(CCl_4)$ 5·7(s, 2H, =CH × 2), 12·3 (s, 1H, OH), 2·6–3·4(m, 5H, CH_2 × 2, CH)
CO_2Et	3070, 1730, 1620, 1200	$\delta_H(CCl_4)$ 5·8(s, 2H, =CH × 2), 4·2 (quartet, 2H, OCH_2), 2·5–3·2(m, 5H, CH_2 × 2, CH), 1·3(triplet, 3H, CH_3)
CO_2Me	3060, 1730, 1620, 1200	$\delta_H(CCl_4)$ 5·7(s, 2H, =CH × 2), 3·8 (s, 3H, OCH_3), 2·5–3·2(m, 5H, CH_2 × 2, CH)

Shimadzu GC-9A with flame ionization detection. In most cases a 3m PEG 20M column (sometimes a SE-30 or a liquid crystal column) was used. In methanol and in ethanol n-butanol or i-pentanol was used as internal standard; in acetic acid generally ethylene glycol diethyl ether (in some cases nitrobenzene or *p*-chlorotoluene) was used. G.l.c. analysis was in triplicate for each competitive experiment. Four independent runs under the same reaction conditions were used to evaluate each relative rate constant together with experimental error. The relative rates, k_A/k_B, were calculated according to the relationship:

$$k_A/k_B = [\log(S_{A,0}/S_{r,0}) - \log(S_A/S_r)]/[\log(S_{B,0}/S_{r,0}) - \log(S_B/S_r)],$$

where $S_{A,0}$ and S_A, $S_{B,0}$ and S_B, $S_{r,0}$ and S_r are initial and final peak areas of olefin A, olefin B and the internal standard. Since it was difficult to separate cyclopentene (H) from the other olefins or solvents by g.l.c. under our working conditions, all rates relative to that of cyclopentene were determined by indirect competition via cyclohexene (ch), i.e. $k_X/k_H = k_X/k_{ch} \times k_{ch}/k_H$. For the relative rates, k_X/k_H, which are less than 0·1, $k_X/k_H = k_X/k_{X'} \times k_{X'}/k_{ch} \times k_{ch}/k_H$. Generally, the experimentally determined relative rates (k_X/k_{ch}, $k_X/k_{X'}$, k_{ch}/k_H) are between 0·1 and 10. Some olefins reacted with the solvents, for example, Δ^3-cyclopentenecarboxylic acid reacted with all three solvents, so in these cases the relative rates could not be measured.

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