PERKIN 2

A kinetic, product and kinetic isotope effect investigation of the bromination of 1,1-diphenylethylenes and of their 2,2-dideuterio derivatives

Giuseppe Bellucci and Cinzia Chiappe*

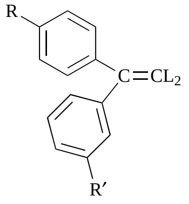
Dipartimento di Chimica Bioorganica, via Bonanno 33, 56126 Pisa, Italy

The kinetics of bromination of 1,1-diphenylethylene (1a), 4-trifluoromethyl-1,1-diphenylethylene (1b), and 1-(3-trifluoromethylphenyl)-1-(4-trifluoromethylphenyl)ethylene (1c) and of their 2,2-dideuterio derivatives have been investigated in 1,2-dichloroethane. The rate law was always second-order in Br_2 and first-order in olefin, with the following k_3: 1a (L = H), 1.7 (0.1) × 10^7; 1b (L = H), 8.0 (0.1) × 10^4; 1c (L = H), 52 (2) $dm^6\ mol^{-2}\ s^{-1}$. Olefin 1a (L = H) gave dibromide 4a and vinyl bromide 3a in a ratio changing from 99:1 at 10^{-2} mol dm^{-3} to 5:95 at 10^{-4} mol dm^{-3} Br_2 and olefin. The k_3 was independent of the reagent concentrations and of the extent of proton loss from the intermediate, showing that the last step was not rate limiting and the formation of the intermediate was completely rate determining. In the whole investigated concentration range, only dibromides 4b and 4c were instead obtained from 1b and 1c, respectively. A negligible KIE, 0.97 (0.01) was found for 1a, whether the dibromide or the vinyl bromide was the main product, while significant inverse KIEs were obtained for 1b, 0.75 (0.05), for 1c, 0.70 (0.05), on deuteriation of the methylene group, and for *cis*-1,2-diphenylethylene, 2. The kinetic and product distribution data are discussed in terms of nature of the intermediates, depending on substituent effect and reagent concentration.

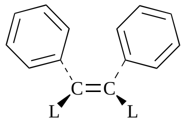
In spite of extensive investigations[1] and the apparent simplicity of olefin bromination, recent studies have revealed new important aspects, which have modified the traditional mechanistic picture of the reaction, and have introduced additional criteria for evaluating structure–reactivity relationships.[2] Product and kinetic studies have shown that the electrophilic step is not necessarily irreversible,[3] but a continuous spectrum of situations ranging from essentially irreversible to prevalent ion reversal appears to exist. Furthermore, kinetic investigations have taken into account the nature of the interaction in olefin–Br_2 complexes,[4] the lifetime of the bromonium ions in MeOH,[5] the importance of solvent assistance[2b,3d,6] and kinetic isotope effects (KIE).[7] In particular, a kinetic criterion for bromonium ion reversal consisting of the observation of a primary KIE by allyl C–D bonds on the bromination rate has been used,[7] but it can be applied only to congested olefins yielding substituted products by loss of a proton from the bromonium ion. A significant inverse KIE has been observed instead[7b] for the bromination in acetic acid of a typical cyclic olefin, cyclohexene, which gives the normal addition products.

Evidence for the reversible formation of bromonium ions arising from uncongested aryl substituted olefins in halogenated solvents was found from a product study.[3f] In particular, it has been shown[3f] that in the bromination of 1,2-diphenylethylenes in 1,2-dichloroethane the reversibility of the olefin–Br_2 charge transfer complexes ionization to ion pairs depends on the bridged or open nature of the cationic moiety, which is determined by the presence of remote ring substituents.

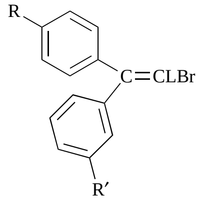
In order to check the occurrence of this substituent effect in the case of the more reactive 1,1-diphenylethylenes, we undertook a combined kinetic and product investigation of the bromination of 1,1-diphenylethylene, **1a**, and of its 4-trifluoromethyl and 3,4′-bis(trifluoromethyl) derivatives, **1b** and **1c**, and of the corresponding 2,2-dideuterio derivatives, in chlorinated solvents. The results have shown that for these olefins the nature of the intermediates, and thus the reversibility, depends on the substituents on the phenyl rings. Furthermore, they have indicated that even secondary kinetic isotope effects could be a mechanistic criterion for evaluating the nature of the intermediates and rate determination during the nucleophilic step in the bromination reactions.



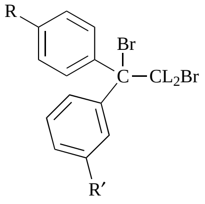
1 (L = H or D)
a: R = R′ = H
b: R = CF$_3$, R′ = H
c: R = R′ = CF$_3$



2 (L = H or D)



3 (L = H or D)
a: R = R′ = H
b: R = CF$_3$, R′ = H
c: R = R′ = CF$_3$



4 (L = H or D)
a: R = R′ = H
b: R = CF$_3$, R′ = H
c: R = R′ = CF$_3$

Results

Olefins **1** (L = H or L = D) were prepared by conventional Grignard methods followed by dehydration of the resulting alcohols. Dibromides **4a–c** were obtained from the corresponding olefins by bromination with $Bu_4N^+Br_3^-$ in 1,2-dichloroethane, in the presence of an excess of $Bu_4N^+Br^-$.[8]

The bromination rates of all the olefins **1a–c** (L = H and L = D) with Br_2 were measured in 1,2-dichloroethane (DCE), at 25 °C, by monitoring the disappearance of the halogen and

Table 1 Third-order rate constants, KIE values and product distribution for the ionic bromination of 1,1-diphenylethylenes and 1,2-diphenylethylenes in 1,2-dichloroethane at 25 °C

Olefin	k_3/ $\mathrm{dm^6\,mol^{-2}\,s^{-1}}$	k_H/k_D	**3**:**4**
1a	1.7 (0.1) × 10^7	0.97 (0.01)	*a*
1b	8.0 (0.1) × 10^4	0.75 (0.05)	1:99
1c	52 (2)	0.70 (0.05)	0:100
2	2.8 (0.1) × 10^2	0.75 (0.05)	

[a] See Table 2

Table 2 Product distribution for the ionic bromination of **1a** in aprotic solvents at 25 °C

1a mol $\mathrm{dm^{-3}}$	Br_2 mol $\mathrm{dm^{-3}}$	Solvent	**3**:**4**
10^{-2}	10^{-2}	$(CH_2Cl)_2$	<1:99
10^{-3}	10^{-3}	$(CH_2Cl)_2$	10:90
5 × 10^{-4}	5 × 10^{-4}	$(CH_2Cl)_2$	60:40
2.5 × 10^{-4}	2.5 × 10^{-4}	$(CH_2Cl)_2$	95:5
10^{-4}	10^{-4}	$(CH_2Cl)_2$	>99:1
10^{-2}	10^{-2}	CH_2Cl_2	<1:99
10^{-3}	10^{-3}	CH_2Cl_2	<1:99
5 × 10^{-4}	5 × 10^{-4}	CH_2Cl_2	40:60
10^{-2}	10^{-2}	$CHCl_3$	<1:99
5 × 10^{-4}	5 × 10^{-4}	$CHCl_3$	<1:99
2.5 × 10^{-4}	2.5 × 10^{-4}	$CHCl_3$	15:85

using a conventional spectrophotometer, or a stopped flow apparatus. All the reactions obeyed the third-order rate law of eqn. (1) and the k_3 value spanned six powers of ten (Table 1).

$$-\mathrm{d}[\mathrm{Br_2}]\,/\,\mathrm{d}t = k_3\,[\text{olefin}][\mathrm{Br_2}]^2 \qquad (1)$$

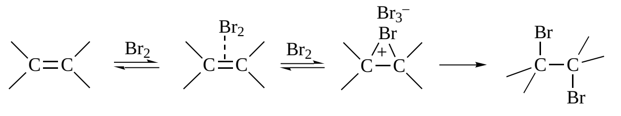
In the case of **1a**, although the product composition changed (see below) with dilution, the k_3 values were practically constant. A negligible KIE, $k_H/k_D = 0.97$ (0.01) was found for the unsubstituted olefin **1a**, but significant inverse KIE were obtained for **1b**, $k_H/k_D = 0.75$ (0.05), and for **1c**, $k_H/k_D = 0.70$ (0.05). An inverse KIE, $k_H/k_D = 0.75$ (0.05), was also measured for the bromination of *cis*-1,2-diphenylethylene, **2**, on replacement of the double bond hydrogens by deuterium.

The ratios of vinyl bromide, **3**, to dibromide, **4**, determined by HPLC and/or NMR for the reactions of Br_2 with olefins **1b–c** in DCE at 25 °C, under conditions identical to those employed for the kinetic measurements, are given in Table 1.

At variance with **1b** and **1c**, which gave, practically, only dibromides **4b** and **4c** (L = H and L = D) at every reagent concentration, the product distribution of the bromination of **1a** showed a dependence on the solvent and reagent concentrations. The vinyl bromide to dibromide ratios, **3**:**4**, obtained by fast mixing of equimolar solutions of **1a** and Br_2 at different concentrations in three aprotic solvents of moderate to low polarity (DCE, dichloromethane and chloroform) are given in Table 2. All the products were quantitatively recovered after exposure to Br_2 assuring that the reported ratios were obtained under kinetic control.

Discussion

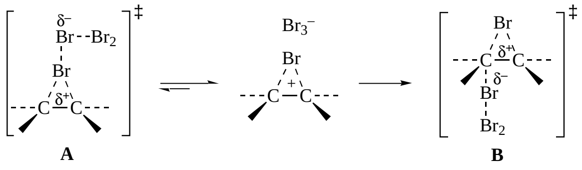
All the results of the kinetic and product distribution study for the third-order process reported in Tables 1 and 2 can be rationalized on the basis of the generally accepted mechanism for the ionic bromination of olefins in aprotic solvents, sketched in Scheme 1, involving the formation of bromonium (or bromocarbonium)–tribromide ion pairs by ionization of the olefin–Br_2 π complex formed in a pre-equilibrium step. Although the intermediate ions can be symmetrically or asymmetrically bridged, or open β-bromocarbonium ions depending on the nature of the substituents on the double bond, for the sake of simplicity, the intermediates are represented in Scheme 1 as fully bridged bromonium ions.



Scheme 1

It has been shown[3f] by product studies that in the bromination of 1,2-diphenylethylenes in 1,2-dichloroethane not only the ratios between the isomeric dibromides but also the reversibility of the ionization of the olefin–Br_2 π complexes to ion pairs, as evidenced by the *cis* ⟶ *trans* isomerization of the unreacted *cis* olefins depends on the bridged or open nature of the cationic moiety. Whereas electron donating substituents favouring open *β*-bromocarbonium ion intermediates give stereoconvergent mixtures of *meso*- and (±) dibromides from both the *cis* and *trans* olefins and depress the reversibility, electron withdrawing groups like CF_3, favouring fully bridged bromonium ions, give stereoselective reactions and make ion pair return very prominent. Furthermore, partially bridged intermediates, always able to revert to reagents, were proposed for the bromination of the unsubstituted *cis* and *trans*-1,2-diphenylethylenes in chlorinated solvents.[3f,9]

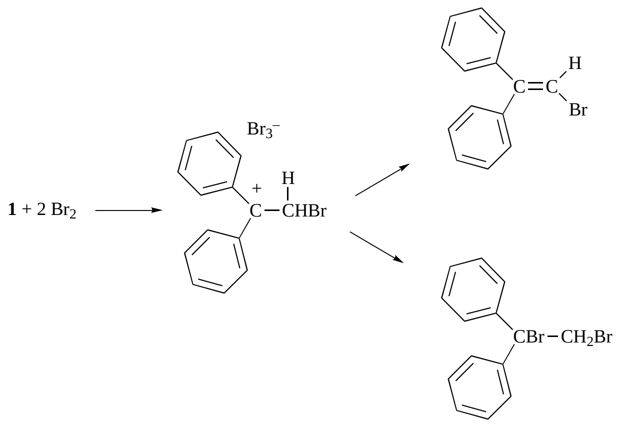
Considering that for *cis*-1,2-diphenylethylene, **2**, the product distribution studies have shown[3f,9] that the ionization step is reversible and the nucleophilic step is at least partially rate determining, the significant inverse KIE found in the present work for this olefin,[10] consistent with a rate determining transition state (rdts) having considerable rehybridization of the double bond carbons from sp^2 towards sp^3, is related not only to the hybridization changes in the transition step leading to the partially bridged intermediate (A, in Scheme 2), but also to the changes occurring in the transition state of the nucleophilic step (B, in Scheme 2). In agreement with the Hammond postulate both the transition states leading to or away from the ionic intermediate are partially bridged. One possible effect of reversibility was postulated[7b] also for the significant inverse KIE found for the bromination of cyclohexene in acetic acid, although the exact reason for the large observed value is, at the moment, unclear. Moreover, as suggested in the same work, a sole rehybridization effect on the formation of bromonium ion could not account for the observed inverse KIE. In fact, these values are significantly larger than those usually observed for addition processes such as Diels–Alder reactions[11] or electrophilic additions to α,β-unsaturated esters[12] in which similar rehybridization occurs.



Scheme 2

In the case of the unsubstituted 1,1-diphenylethylene, **1a**, however, the bromination probably occurs *via* a carbonium-like-transition state through the irreversible formation of an open β-bromocarbonium ion for which collapse to dibromide competes with proton elimination.

The constant k_3 value found at different reagent concentrations, when the product distribution changes from dibromide to vinyl bromide, points in fact to a substantially irreversible π complex ionization step. Furthermore, also consistent with this hypothesis is the lack of a large primary KIE expected for a slow L^+ loss when the vinyl bromide is the main product. Taking into account that in this case the rate determining step is the



Scheme 3

formation of a bromocarbonium–tribromide ion pair and that the transition state should be closely related to the intermediate,[2b] the apparent lack of even a secondary effect is probably due to a compensation of the inverse KIE produced by the hybridization change at the methylene carbon during the ionization step by a normal effect, of comparable magnitude, due to hyperconjugative interaction of the carbonium centre with the β-C–L bonds. The β-effect can be the same or sometimes even greater than the α-effect (1.1–1.3 per deuterium).[13]

Significant inverse KIE were instead observed in the ionic bromination of **1b** and **1c**, and taking into account the kinetic and product distribution data related to the bromination of *cis*-1,2-diphenylethylene, a probable involvement of at least partially bridged intermediates, susceptible to return to reagents, can be proposed for the bromination of these two deactivated 1,1-diphenylethylenes. Moreover, the different nature of the intermediates arising from **1a** with respect to **1b** and **1c** can also explain the different product distribution observed in the bromination of these olefins, *i.e.* only dibromides from **1b** and **1c**, and mixtures of dibromide and vinyl bromide from **1a**. Open β-bromocarbonium ions, involved in the bromination of **1a**, could more easily undergo proton loss than the bridged ones.

On the other hand, the concentration and solvent effect on the vinyl bromide to dibromide ratio found for **1a**, could be related to the degree of ion pair dissociation. A progressive change from tight to solvent-separated ion pairs and, perhaps, to free ions may occur, in particular in the more polar dichloromethane and DCE, around the lowest reagent concentrations, when the concentration of the intermediates should be reduced, too. The ion pair dissociation could disfavour the rapid collapse of the counteranion with the carbocation making the fast removal a β proton by a base competitive. It is possible that the geometric requirements for dibromide formation or elimination are different and that the barrier for interconversion of the different types of ion pairs is smaller in the solvent separated than in the tight ion pairs. Since proton loss from the intermediate implies probably Br^- as a base, also consistent with the data could be the dilution effect on the ability of Br_3^- to give Br^- *via* the Br_2–Br_3^- equilibrium ($[Br^-] = [Br_3^-]/K[Br_2]$). On the other hand, although ion pair dissociation also occurs in chloroform,[9] at least at very low reagent concentrations, and the counteranion is in this case essentially Br^-, this is hydrogen bonded to the solvent.[9] The solvation of the counteranion in chloroform could then reduce its basicity and favour the formation of dibromide over proton loss.

In conclusion, the present data show that the ionization step is rate determining in the bromination of **1a**, whose intermediate is an open β-bromocarbonium ion, and suggest that the product forming step becomes at least partially rate determining (*i.e.* the ionic intermediates are reversibly formed) with the CF_3 substituted olefins **1b** and **1c**, where the cationic intermediates are partially or fully bridged ions, in analogy to the bromination of the corresponding 1,2-diphenylethylene derivatives. Furthermore, the comparison of the KIE determined for the bromination of **1a** with those related to **1b**, **1c** and in particular to **2**, for which product distribution data have been used to show that the ionic intermediate is formed reversibly, suggests that even the secondary kinetic isotope effects could be a mechanistic criterion for evaluating the nature of the intermediates and rate determination during the nucleophilic step of the bromination reactions.

Experimental

Melting points were determined on a Kofler apparatus and are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker AC 200 instrument containing $SiMe_4$ as the internal reference. *J* values are in Hz. HPLC analyses were carried out with a Waters 600E apparatus equipped with a diode array detector using a Spherisorb S5CN column, 25 cm, with hexane–tetrahydrofuran (THF) (99 : 1 v/v) as the eluent, at a flow rate of 1 ml min^{-1}. Kinetic measurements were performed with a Cary 2200 spectrophotometer or with a Durrum D-110 stopped flow instrument.

Bromine (1 ml sealed ampoules, C. Erba > 99.5%) and 1,2-dichloroethane (Fluka ⩾ 99.5%) were used as supplied.

Olefins

Olefins **1b** and **1c** (L = H) were prepared by reacting methylmagnesium bromide with 4-(trifluoromethyl)benzophenone and 3,4′-bis-(trifluoromethyl)benzophenone, respectively, followed by dehydration with toluene-*p*-sulfonic acid in refluxing benzene. Olefins **1a–c** (L = D) were obtained with the same procedure using CD_3MgI. ^{1}H NMR analysis indicated the presence of *ca.* 2% of H at the vinylic position. Olefin **2** (L = D) was prepared as previously reported.[14] ^{1}H NMR analysis indicated the presence of *ca.* 10% of H at the vinylic positions. Commercial 1,1-diphenylethylene (Aldrich, 97%) and *cis*-stilbene (Aldrich > 97%) were distilled before use. All olefins were finally checked by HPLC and NMR and were found to be > 99% pure.

1a (L = D) Oil, $\delta_H(CDCl_3)$ 7.35 (m, ArH).

1b (L = H) Oil, $\delta_H(CDCl_3)$ 5.50 (d, 1 H, *J* 1, $=CH_2$); 5.55 (d, 1 H, *J* 1, $=CH_2$) 7.35 (m, 5 H, ArH); 7.40–7.60 (AA′BB′ system, 4 H, ArH). Anal. Calc. for $C_{15}H_{11}F_3$: C, 72.57; H, 4.47. Found: C, 72.45; H, 4.45%.

1b (L = D) Oil, $\delta_H(CDCl_3)$ 7.35 (m, 5 H, ArH); 7.40–7.60 (AA′BB′, 4 H, ArH).

1c (L = H) Oil, $\delta_H(CDCl_3)$ 5.60 (s, 2 H, $=CH_2$); 7.40–7.60 (m, 8 H, ArH). Anal. Calc. for $C_{16}H_{10}F_6$: C, 60.77; H, 3.19. Found: C, 60.70; H, 3.15%.

2 (L = D) Oil, $\delta_H(CDCl_3)$ 7.40–7.60 (m, ArH).

Olefin **3a** was obtained from the corresponding dibromide **4a** by dehydrobromination with NaOH (1 mol dm^{-3}) in THF–H_2O at room temp. Oil δ_H 6.77 (s, 1 H, =CHBr); 7.15–7.45 (m, 10 ArH). δ_C 105.17 (=CH); 127.52, 127.88, 128.03, 128.14, 128.33, 129.57 (ArCH); 138.95, 140.58, 146.69 (quaternary C). Anal. Calc. for $C_{14}H_{11}Br$: C, 64.89; H, 4.28. Found: C, 64.85; H, 4.20%.

Dibromides 4

Olefins **1a–c** were brominated with $Bu_4N^+Br_3^-$ in 1,2-dichloroethane by the reported procedure.[3b]

4a Oil; δ_H 4.50 (s, 2 H, CH_2Br), 7.30–7.60 (m, 10 H, ArH). Anal. Calc. for $C_{14}H_{12}Br_2$: C, 49.45; H, 3.56. Found: C, 49.55; H, 3.45%.

4b Oil; δ_H 4.40–4.50 (AB, 2 H, *J* 11, CH_2Br); 7.45–7.50 (m, 5 H, ArH); 7.60–7.77 (AA′BB′ system, 4 × ArH). Anal. Calc. for $C_{15}H_{11}F_3Br_2$: C, 44.15; H, 2.72. Found: C, 44.23; H, 2.75%.

4c Oil; δ_H 4.45–4.55 (AB, 2 H, *J* 11, CH_2Br); 7.45–7.85 (m, 8 × ArH). Anal. Calc. for $C_{16}H_{10}F_6Br_2$: C, 40.37; H, 2.12. Found: C, 40.55; H, 2.25%.

Bromination procedure

Solvent and concentration dependence of product distribution in the ionic bromination of 1a–c. 1,2-Dichloroethane, dichloromethane or chloroform solutions of Br_2 (0.5 cm^3) of concentration ranging between 1.1×10^{-1} and 1.35×10^{-3} mol dm^{-3} were rapidly mixed with 5 cm^3 of 2.2×10^{-2} to 2.75×10^{-4} mol dm^{-3} solutions of olefins **1** in the same solvent, and the reaction mixtures were stored in the dark at 25 °C. At the end of the reactions, after evaporation of the solvents, or after stopping the reaction by washing with saturated aqueous $NaHSO_3$, the mixtures were analysed by NMR and HPLC. The **3**:**4** ratios were determined by HPLC using appropriate calibration curves and by NMR on the basis of the vinyl and benzyl signals. All the reactions were carried out in triplicate. The ratios reported in Tables 1 and 2 were reproducible within ±2%. All the product ratios were independent of the percentage conversion. The stability of dibromides **4a**–**c** in the presence of the halogen was checked by exposing all dibromides to Br_2 under conditions identical with those employed in the bromination reactions, followed by HPLC or NMR analysis.

Kinetic measurements and product analysis. Solutions of Br_2 in 1,2-dichloroethane, prepared shortly before use, were protected from the daylight and adjusted to twice the desired initial concentrations in the kinetic runs. Aliquots of these solutions, prethermostatted at 25 ± 0.05 °C, were mixed with equal volumes of prethermostatted solutions of olefins **1** of suitable concentrations. The brominations of **1c** and **2** were carried out with the conventional spectrophotometer, those of **1a**–**b** with the Durrum stopped-flow apparatus. The following olefin and Br_2 concentrations (mol dm^{-3}), pathlength (cm), monitored wavelengths (nm) were used: **1a** (L = H or D): 5×10^{-3}–5×10^{-4} and 5×10^{-3}–5×10^{-4}, 2, 480 and 410. **1b** (L = H or D): 5×10^{-3}–5×10^{-4} and 5×10^{-3}–5×10^{-4}, 2, 480 and 410. **1c** (L = H or D): 5–2×10^{-2} and 2.5–1×10^{-3}, 1, 410. **2** (L = H or D): 2×10^{-2}–2×10^{-3} and 2×10^{-3}, 1, 410. The absorbance *vs.* time data were fitted to the appropriate third-order or pseudo-second-order equations. All reactions were carried out at least in triplicate. The kinetic constants are reported in Table 1.

At the end of the reactions, after evaporation of the solvent, all reaction mixtures were analysed by NMR and HPLC. The products were quantified using appropriate calibration curves.

Acknowledgements

This work was supported in part by grants from Consiglio Nazionale delle Ricerche (CNR, Roma) and Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST, Roma).

References

1 (*a*) G. H. Schmid and D. G. Garrat, *The Chemistry of Double-Bonded Functional Groups*, ed. S. Patai, Wiley, New York, 1977; Suppl. A, Part 2, p. 725; (*b*) P. B. D. De la Mare and R. Bolton, *Electrophilic Additions to Unsaturated Systems*, Elsevier, New York, 2nd edn., 1982, p. 136; (*c*) K. A. V'yunov and A. Guniak, I., *Russ. Chem. Rev.* (*Engl. Trans.*), 1981, **50**, 151.

2 For recent reviews see: (*a*) G. H. Schmid, *The Chemistry of Double-Bonded Functional Groups*, ed. S. Patai, Wiley, New York, 1989; suppl. A, vol. 2 pt. 1, p. 699; (*b*) M. F. Ruasse, *Adv. Phys. Org. Chem.*, 1993, **28**, 207.

3 (*a*) R. S. Brown, R. Gedye, H. Slebocka-Tilk, J. M. Buschek and K. R. Kopecky, *J. Am. Chem. Soc.*, 1984, **106**, 4515; (*b*) G. Bellucci, C. Chiappe and F. Marioni, *J. Am. Chem. Soc.*, 1987, **109**, 515; (*c*) G. Bellucci, R. Bianchini, C. Chiappe, F. Marioni and R. Spagna, *J. Am. Chem. Soc.*, 1988, **110**, 546; (*d*) M. F. Ruasse, S. Motallebi and B. Galland, *J. Am. Chem. Soc.*, 1991, **113**, 3440; (*e*) G. Bellucci, C. Chiappe, F. Marioni and F. Marchetti, *J. Phys. Org. Chem.*, 1991, **4**, 387; (*f*) G. Bellucci, R. Bianchini, C. Chiappe, R. S. Brown and H. Slebocka-Tilk, *J. Am. Chem. Soc.*, 1991, **113**, 8012; (*g*) G. Bellucci, R. Bianchini, C. Chiappe, R. Ambrosetti, D. Catalano, A. J. Bennet, H. Slebocka-Tilk, M. G. H. Aarts and R. S. Brown, *J. Org. Chem.*, 1993, **58**, 3401; (*h*) C. Y. Zheng, H. Slebocka-Tilk, R. W. Nagorski, L. Alvarado and R. S. Brown, *J. Org. Chem.*, 1993, **58**, 2122; (*i*) R. W. Nagorski, H. Slebocka-Tilk and R. S. Brown, *J. Am. Chem. Soc.*, 1994, **116**, 419.

4 G. Bellucci, C. Chiappe, R. Bianchini, D. Lenoir and R. Herges, *J. Am. Chem. Soc.*, 1995, **117**, 12001.

5 R. Nagorski and R. S. Brown, *J. Am. Chem. Soc.*, 1992, **114**, 7773.

6 M. F. Ruasse, *Acc. Chem. Res.*, 1990, **23**, 87.

7 (*a*) R. S. Brown, H. Slebocka-Tilk, A. J. Bennet, G. Bellucci, R. Bianchini and R. Ambrosettil *J. Am. Chem. Soc.*, 1990, **112**, 6310; (*b*) H. Slebocka-Tilk, C. Y. Zheng and R. S. Brown, *J. Am. Chem. Soc.*, 1993, **115**, 1347; (*c*) G. Bellucci, R. Bianchini, C. Chiappe, D. Lenoir and A. Attar, *J. Am. Chem. Soc.*, 1995, **117**, 6243.

8 L. F. Fieser, *J. Chem. Educ.*, 1954, **31**, 291.

9 R. Bianchini and C. Chiappe, *J. Org. Chem.*, 1992, **57**, 6474.

10 A KIE = 0.91 has been previously reported for *trans*-1,2-diphenyl$[^2H_2]$ethylene in diethyl ether: D. B. Denny and N. Tunkel, *Chem. Ind.* (*London*), 1959, 1383.

11 J. J. Gajewski, K. B. Peterson, J. R. Kagal and Y. C. Huang, *J. Am. Chem. Soc.*, 1989, **111**, 9078.

12 Y. Elemes and C. S. Foote, *J. Am. Chem. Soc.*, 1992, **114**, 8044.

13 F. Ruff and I. G. Csimadia, *Organic Reactions, Equilibria, Kinetics and Mechanism*, Elsevier, New York, 1994, pp. 233–236.

14 E. C. Ashby and J. J. Lin, *J. Org. Chem.*, 1978, **43**, 2567.

Paper 6/05390D
Received 1*st August* 1996
Accepted 28*th October* 1996