Concentration Dependence of the Steric Course of the Bromine Addition to Arylalkenes. The Case of Stilbenes

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The ratios of *meso*- to *d,l*-1,2-dibromo-1,2-diphenylethane obtained in the bromination of *cis*- and *trans*-stilbene in 1,2-dichloroethane have been determined by HPLC as a function of the reagent concentrations. With stoichiometric reagents both reactions were nonstereoselective down to 10^{-3} M concentrations, but became stereospecific and stereoconvergent to give the meso dibromide at $[Br_2] \leq 2 \times 10^{-3}$ M and 100-fold lower olefin concentration. Kinetic measurements have shown that under all conditions the reaction was occurring through the same rate-determining step. A rationalization, involving tight or solvent-separated ion-pair intermediates, is proposed.

The mechanism of the electrophilic bromination of olefins has been the object of extensive investigations.[1] The stepwise nature of the reaction and the ionic character of the intermediates have been recognized for many years and have recently been conclusively confirmed by the X-ray diffraction characterization of a stable bromonium-tribromide salt formed in the reaction of adamantylideneadamantane with Br_2.[2] The involvement of olefin-Br_2 charge-transfer complexes prior to the rate-determining step leading to the ionic intermediates has been definitely established,[3,4] and evidence for the reversibility of this step has recently been produced.[5,6] The implications of these findings in the reactivity of olefins toward bromination have been discussed.[4-7]

Several factors appear to be implicated in the product-determining step, a few of which are not completely clear. Much attention has been turned to the structure of the cationic moiety of the ionic intermediates, while the nature of the counteranion has generally been overlooked. Thus, the exclusive anti addition found in the bromination of unconjugated olefins is generally considered to be the consequence of the formation of fully bridged bromonium ion intermediates,[8] while the attainment of both anti and syn dibromo adducts from aryl alkenes is attributed to the intermediate formation of weakly bridged or open bromocarbonium ions. Syn addition to these conjugated olefins is considered to occur either by direct syn collapse[9] or, in the case of acyclic aryl olefins, by rotation-translocation followed by anti collapse of the unbridged intermediate ion pairs.[10]

The bridged or unbridged nature of the cationic moiety has been related to the solvent polarity, which should thus influence the syn to anti addition ratio.[5,11,12] Solvent independence of the charge distribution in transition states and intermediates has been, on the other hand, postulated on the basis of the absence of nucleophilic assistance in the bromine addition to olefins in protic solvents, and solvent effects have been suggested to lie rather in the competition between conformational equilibration and nucleophilic trapping of the intermediates.[13,14] Ring

Table I. Distribution of *meso*- and *d,l*-1,2-Dibromo-1,2-diphenylethane in Brominations of *cis*- and *trans*-Stilbene in 1,2-Dichloroethane at 25 °C

run	$[Br_2]$, M	[1], M	[2], M	% dibromide 3	% dibromide 4
1	2×10^{-1}	2×10^{-1}		50	50
2	2×10^{-2}	2×10^{-2}		49	51
3	2×10^{-3}	2×10^{-3}		54	46
4	1×10^{-3}	1×10^{-3}		53	47
5	2×10^{-2}	2×10^{-1}		47	53
6	4×10^{-3}	4×10^{-2}		52	48
7	1×10^{-3}	1×10^{-2}		49	51
8	2×10^{-1}	2×10^{-2}		52	48
9	2×10^{-2}	2×10^{-3}		53	47
10	8×10^{-3}	8×10^{-4}		56	44
11	4×10^{-3}	4×10^{-4}		62	38
12	2×10^{-3}	2×10^{-4}		80	20
13	1×10^{-3}	1×10^{-4}		82	18
14	2×10^{-2}	2×10^{-4}		62	38
15	4×10^{-3}	4×10^{-5}		78	22
16	2×10^{-3}	2×10^{-5}		96	4
17	1×10^{-3}	1×10^{-5}		96	4
18	2×10^{-2}	2×10^{-5}		68	32
19	2×10^{-1}		2×10^{-1}	68	32
20	2×10^{-2}		2×10^{-2}	67	33
21	2×10^{-3}		2×10^{-3}	71	29
22	1×10^{-3}		1×10^{-3}	70	30
23	2×10^{-2}		2×10^{-3}	72	28
24	8×10^{-3}		8×10^{-4}	78	22
25	4×10^{-3}		4×10^{-4}	84	16
26	2×10^{-3}		2×10^{-4}	94	6
27	8×10^{-4}		8×10^{-5}	95	5
28	2×10^{-2}		2×10^{-4}	78	22
29	8×10^{-3}		8×10^{-5}	82	18
30	4×10^{-3}		4×10^{-5}	88	12
31	2×10^{-3}		2×10^{-5}	96	4
32	8×10^{-4}		8×10^{-6}	96	4

(1) For extensive recent review of olefin brominations, see: Schmid, G. H.; Garrat, D. G. *The Chemistry of Double Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York; Suppl. A., Part 2, p 725. V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 151. De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982; pp 136-197.

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(12) Heublein, G. *Prakt. Chem.* **1966**, *31*, 84.

(13) Ruasse, M.-F.; Dubois, J.-E. *J. Am. Chem. Soc.* **1975**, *97*, 1977.

(14) For a discussion of the effect of a change in solvent from the apolar carbon tetrachloride to methanol on the transition-state structure of stilbene bromination (defined as bromonium-like in the first solvent, carbonium-like in the second), see, however, ref 15b.

substituents have been shown to determine the competition between bromonium and carbonium ion pathways in the bromination of trans stilbenes.[15]

Occasional reports also indicate that the dibromide ratios obtained from phenyl-substituted olefins, like stilbenes[12] and methyl *p*-methyl-*trans*-cinnamate,[16] depend on the mode of addition and on the concentration of Br_2. Furthermore, changes in the syn to anti and 1,2- to 1,4-dibromo adduct ratios by using very diluted Br_2 have been reported in the addition to conjugated dienes in apolar solvents.[17] Different kinetic orders in different Br_2 concentration regions, involving different rate-determining steps and leading to different intermediates, have been suggested, but not conclusively proved, in order to rationalize these findings.[16]

In this paper we now report the results of a systematic investigation of the effects of the reagent concentrations on the steric course of the bromination of *cis*- and *trans*-stilbene in a low polarity aprotic solvent, 1,2-dichloroethane. On the basis of these results we propose a new rationalization, involving tight or solvent-separated ion pair intermediates in the product-determining step of these reactions.

Results

Product Distributions. The ratios of meso to *d,l* dibromide (**3** and **4**) determined by HPLC for the bromination of *cis*- and *trans*-stilbene (**1** and **2**) in 1,2-dichloroethane at 25 °C are reported in Table I. The reactions were carried out by fast mixing the entire amounts of the required solutions of the two reagents. Both stoichiometric reactions and runs in which one component was in large excess, so that its concentration remained practically unchanged during the entire course of the reaction, were examined. Products were usually analyzed after 3 h, a time required to brominate about 65% of olefin in run 4 of Table I, but checks at shorter times were also performed.

The 1:1 reactions of *cis*-stilbene were completely lacking in stereoselectivity down to 10^{-3} M reagent concentrations (runs 1–4 of Table I). Identical results were obtained in reactions performed with a 10-fold excess of olefin (runs 5–7). The runs carried out with excess Br_2 exhibited instead a progressive increase in the **3**:**4** ratio with decreasing reagent concentrations. However, this effect appeared only at $[Br_2] < 10^{-2}$ M in reactions performed with a 10:1 ratio of Br_2 to **1**, while it was already observed at 2×10^{-2} M $[Br_2]$ in 100:1 and even more markedly in 1000:1 reactions (compare runs 9, 14, and 18). Furthermore, for similar sets of Br_2 concentrations, the lower the olefin concentration, the higher was the **3**:**4** ratio (compare runs 9–13 and runs 14–17). In the bromination of **1** with a 100-fold excess of Br_2 the steric course changed from completely nonstereoselective at $[Br_2] > 2 \times 10^{-2}$ M to nearly completely syn stereospecific at $[Br_2] \leq 2 \times 10^{-3}$ M. On the other hand, for equal olefin concentrations, the lower was $[Br_2]$, the higher was the **3**:**4** ratio (compare runs 12 and 14 and runs 16 and 18).

Dibromides **3** and **4** were found to be stable under the bromination conditions. Both were quantitatively recovered from 10^{-4} to 10^{-2} M 1,2-dichloroethane solutions in the presence of a large excess of Br_2 after 3 h, thus excluding any dibromide interconversion.

The previously observed[5] rearrangement of *cis*- to *trans*-stilbene during the bromination was confirmed in this investigation. Runs 3 and 4 were followed by monitoring the Br_2 absorbance spectrophotometrically up to about 90% reaction and by determining the product distribution at several times by HPLC. A maximum 6–8% amount of *trans*-stilbene was found in the latest stages of the reactions, and the **3**:**4** ratio remained constant, in agreement with the previous report.[5] The trans olefin detected at the end of run 7, carried out with a 10-fold excess of *cis*-stilbene, was 5% of the unreacted cis isomer. The maximum amount of *trans*-stilbene detected during the progress of run 13, leading to a large excess of meso dibromide **3**, was 16% of the total products, and again the **3**:**4** ratio did not change significantly up to about 90% reaction. Run 17 was also analyzed after a 10-min reaction time. A 10% of the trans olefin and 20% of meso dibromide, with less than 1% of the *d,l* isomer, were found besides the unreacted cis olefin.

Trends of dibromide ratio completely similar to those found for the bromination of *cis*-stilbene were observed in the analogous reactions of the trans olefin. In stoichiometric reactions about 7:3 mixtures of dibromides **3** and **4** were obtained, independently of the reagents concentrations down to 10^{-3} M (runs 19–22), but this ratio increased with decreasing $[Br_2]$ in reactions carried out with a 10:1 and even more with a 100:1 ratio of Br_2 to **2** (runs 23–27 and 28–32). Again, the meso:*d,l* ratio raised both with decreasing olefin concentration at constant $[Br_2]$ (compare runs 23 and 28) and with decreasing $[Br_2]$ at constant [**2**] (compare runs 26 and 28 and runs 27 and 29). No change in this ratio was observed during single runs. No isomerization of *trans*- to *cis*-stilbene was ever detected. At $[Br_2]$ 2×10^{-3} M and 100-fold lower olefin concentration the reactions of *trans*- and *cis*-stilbene became stereoconvergent.

cis- and *trans*-stilbene were also brominated in a nonprotic polar solvent, nitromethane, at 10^{-2} M Br_2 and 10^{-3} M olefin. The meso and *d,l* dibromide were obtained in ratios of 70:30 and 90:10, respectively.

Kinetic Measurements. The kinetics of bromination of *cis*- and *trans*-stilbene in 1,2-dichloroethane had been investigated[5] at 2.5×10^{-3} M concentration of both reagents and shown to be overall third-order, first-order in olefin and second-order in Br_2.

To check if changes in the rate-determining step were occurring in reactions carried out at different reagent concentrations and ratios, kinetic measurements were performed with a 1:1 reagent ratio at 2×10^{-2} and 1×10^{-3} M concentrations, at 5×10^{-4} M Br_2 with excess olefin, and at 1×10^{-4} M olefin with excess Br_2. *cis*-Stilbene was used as the olefin, since it exhibited larger product changes with decreasing reagent concentrations (see Table I). At 2×10^{-2} M concentration of both reagents, the reaction required the use of the stopped-flow technique, whereas at the other investigated concentrations it was slow enough to be followed in a conventional spectrophotometer, monitoring the disappearance of Br_2. Of course, reactions carried out with a large excess of Br_2 could not be monitored in this way. The HPLC technique was used in the latter case to analyze samples withdrawn at time intervals. Runs 1 and 2 of Table II were found to obey very cleanly a third-order rate law, with k_3 values in good agreement with the previously reported one, $k_3 = 270 \pm 10$ M^{-2} s^{-1}.[5] A $k_3 = 49.5 \pm 2.5$ M^{-2} s^{-1} had been found[5] for the trans isomer **2**. In runs 3 and 4 the disappearance of Br_2 and

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Table II. Rate Constants for the Bromination of *cis*-Stilbene in 1,2-Dichloroethane at 25 °C at Different Reagent Concentrations

run	$[Br_2]$, M	[1], M	k_3, M^{-2} s^{-1} [a]
1[b]	2.0×10^{-2}	2.0×10^{-2}	300 (10)
2[c]	1.0×10^{-3}	1.0×10^{-3}	280 (5)
3[c]	5.0×10^{-4}	8.0×10^{-3}	285 (5)
4[d]	1.0×10^{-3}	1.0×10^{-4}	320 (10)

[a] Errors are given as standard deviations estimated from the deviations of experimental points from the best fit third-order (runs 1 and 2), pseudo-second-order (run 3), or pseudo-first-order (run 4) straight lines. [b] Reaction followed by monitoring the disappearance of Br_2 at 530 nm in a stopped-flow apparatus. [c] Reaction followed by monitoring spectrophotometrically the disappearance of Br_2 at 409 nm. [d] Reaction monitored by HPLC.

that of 1 cleanly fitted respectively a pseudo-second-order and a pseudo-first-order rate law. Assuming an overall third-order dependence in all runs, the k_3 values reported in Table II were obtained. The constancy of these k_3 assured that under all investigated conditions, covering a 2×10^{-2} to 5×10^{-4} M range of Br_2 concentration, no change was occurring in the rate determining step, even when largely different dibromide ratios were obtained (compare runs 1 and 4 of Table II, giving the product distributions of runs 2 and 13 of Table I).

Discussion

The stability of the meso and *d,l* dibromide under the reaction conditions and the constancy of their ratios during each single run of the stilbenes bromination exclude the possibility that the changes in product distributions with changing reagent concentrations were due both to dibromide isomerization and to olefin isomerization. The amounts of trans olefin formed during the bromination of *cis*-stilbene are certainly far from sufficient to account for the stereoconvergent reactions of the two olefins at the lowest reagent concentrations, since this would require complete conversion of the cis to trans olefin. In any case, the concentration dependence of the stereochemical outcome of the bromination of *trans*-stilbene, and its antistereospecificity only at sufficiently high dilution, would be rationalized. Furthermore, in incomplete *cis*-stilbene brominations, or in runs using a large olefin excess, the dibromide ratio could hardly be affected by the formation of the trans olefin, since the latter has a k_3 5-fold lower relative to the former olefin, from which dibromides are therefore mainly produced.[5]

The kinetic measurements of Table II also exclude the fact that the observed concentration dependence of the product distribution could be due to the formation of different intermediates through reactions of different kinetic orders, as suggested for the bromination of methyl *p*-methyl-*trans*-cinnamate,[16] and are always consistent with a Br_2-assisted ionization of olefin–Br_2 charge-transfer complexes to give cationic intermediates having a tribromide counteranion.[5]

The structure of the transition state and the resulting intermediates in the bromination of aryl olefins has been the object of debate. A single bromonium-ion-like transition state, leading to either bridged or open cationic intermediates, depending on the nature of the attached groups, has been suggested by a thermochemical–kinetic approach for the electrophilic bromination of olefins, including *cis*- and *trans*-stilbene.[18] A multipathway scheme, in which each type of intermediate is generated in a discrete pathway involving a distinct transition state, with the positive charge developed either on carbon or on bromine, has been proposed instead on the basis of structure–reactivity relationships for the bromination of trans stilbenes in methanol.[15] Carbonium and bromonium ion pathways have been reported to give comparable contributions in the bromination of unsubstituted *trans*-stilbene.[15c] Whichever may be the nature (single or multiple) of the transition state in 1,2-dichloroethane, the involvement of carbonium ion pathways, besides bromonium ion pathways, is shown by the moderate antistereoselectivity and by the complete lack of stereoselectivity respectively observed in the bromination of *trans*- and *cis*-stilbene at relatively high reagent concentrations. However, the continuous increase in the 3:4 ratio, resulting in practically stereospecific and stereoconvergent reactions at sufficiently low concentrations, indicates a progressive change in the nature or mode of collapse of the ionic intermediates.

In principle, the anionic moiety could be involved in this change when the Br_2 concentration is varied. We have recently shown[19] that, in the solvent used in the present investigation, tetrabutylammonium pentabromide is formed from the corresponding tribromide and Br_2 with a $K_f = 14.3$ M^{-1} at 25 °C. We have further demonstrated, using the adamantylideneadamantane–Br_2 system,[4] that this tribromide–pentabromide equilibrium holds also when the cation is a bromonium ion. A similar constant, $K_f = 22.4$ M^{-1}, was obtained for the formation of adamantylideneadamantane bromonium ion–pentabromide from the corresponding tribromide and Br_2.[4] These findings show that the ionic intermediates formed during the third-order bromination of olefins in low-polarity aprotic solvents like 1,2-dichloroethane must undergo a very fast equilibration of the counteranion according to eq 1,[20] the relative

$$\text{Br}^+\text{Br}_3^- + \text{Br}_2 \rightleftharpoons \text{Br}^+\text{Br}_5^- \qquad (1)$$

amounts of the Br_3^- and Br_5^- species being determined by the concentration of Br_2.

It has been conjectured[19] that this may be one of the reasons for the variations in the distribution of bromination products with the halogen concentration. From the above reported K_f value for a bromonium–pentabromide salt it can be inferred that only at $[Br_2] > 10^{-2}$ M should the fraction of the intermediate in the Br_5^- form exceed 20%. However, the present data show that with both *cis*- and *trans*-stilbene the change in the dibromide distribution occurs essentially below this halogen concentration, that is, in a region where the Br_3^- form is always largely predominant. Thus, an equilibrium of type 1, involving either bromonium or bromocarbonium ions or both as the cationic moieties, could be responsible for the product changes observed at constant olefin concentration and variable $[Br_2]$ only if a nonstereoselective collapse of the ion pair in the pentabromide form is considerably faster than that of the tribromide form.

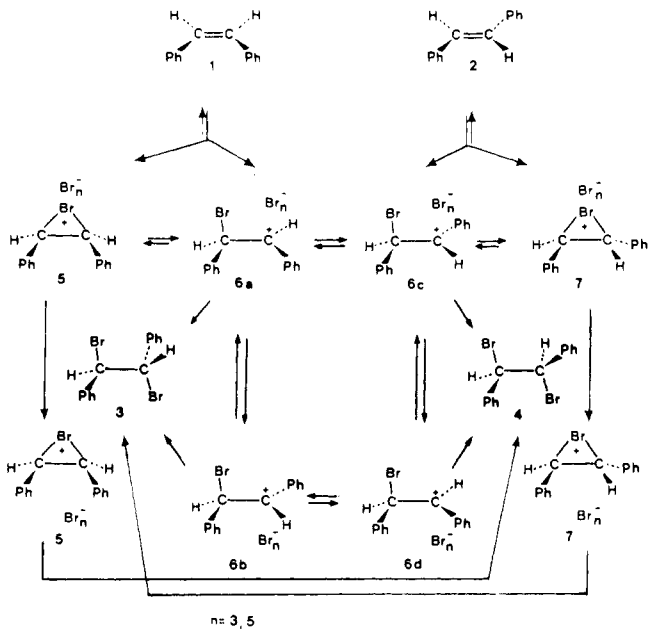
Furthermore, the tribromide–pentabromide equilibrium cannot account for the changes in the dibromide ratio observed in runs carried out at the same $[Br_2]$ but with different reagent ratios. These changes clearly show that not only the halogen concentration, but also the olefin concentration, is crucial in determining the product distribution, and suggest that the evolution of the interme-

(18) Yates, K.; McDonald, R. S. *J. Org. Chem.* **1973**, *38*, 2465.

(19) Bellucci, G.; Bianchini, R.; Chiappe, C.; Ambrosetti, R. *J. Am. Chem. Soc.* **1989**, *111*, 199.

(20) This counteranion equilibration is shown in eq 1 for a bromonium intermediate, but certainly holds also for a bromocarbonium ion intermediate.

Scheme I



diates to products is related to their concentration.

The bromonium and carbonium ion pathways for the bromination of *cis*- and *trans*-stilbene are shown in Scheme I, where the open-ion intermediate can equilibrate between forms **6a–d** by rotation around the C–C bond, and translocation of the anion and the nature of the anion (Br_3^- or Br_5^-) depends on the Br_2 concentration, as discussed above. While the cis and trans bromonium ions **5** and **7** can only collapse to the *d,l* and meso dibromide **4** and **3**, respectively, the carbonium ion intermediate **6** can lead to both **3** and **4** if its equilibration is fast relative to its rate of collapse to product.

In the employed low-polarity aprotic solvent the ionic intermediates are surely formed in the rate-determining step as tight ion pairs. While rotation around the C–C bond is probably always fast, translocation of the counteranion can be slow in these tight ion pairs, since an increase in the distance of the two electrostatically bound ions should occur during this process.[21] Thus, **6a** ⇄ **6b** and **6c** ⇄ **6d** may roughly behave as diastereoisomeric ion pairs, leading essentially to dibromides **3** and **4** from *cis*- and *trans*-stilbene, respectively, and the **3**:**4** ratio should roughly reflect the relative contributions of the bromonium and carbonium ion pathways for the trans olefin and vice versa for the cis isomer.

On the other hand, the ion pair association–dissociation being an equilibrium process, when at least one of the reagents is sufficiently diluted, the concentration of the formed ion pairs could become so low that, even if their dissociation constant is low in low-polarity solvents,[22] they may dissociate to solvent-separated ion pairs. Under these conditions any diastereoisomeric differentiation between the open intermediates would be lost, and the amount of dibromide **3** should increase as the consequence of a preferential anti collapse of the most thermodinamically stable conformer **6b**.

This rationalization cannot, however, completely account for the stereoconvergent and nearly stereospecific bromination of both stilbenes, since the same result should be obtained at any reagent concentration in a polar solvent like nitromethane, where solvent-separated ion pairs are almost surely involved,[22] in contrast with the results presently obtained in this solvent. Furthermore, the above rationalization would completely exclude for the bromination of *cis*-stilbene the bromonium ion pathway, which is instead considered to be mainly responsible for the formation of the *d,l* dibromide under conditions favoring tight over solvent-separated ion pairs. In our opinion, the present results suggest an equilibration of *all* intermediates when they are present *as solvent-separated ions pairs in low-polarity solvents*.[23] More bridging is likely to be present under these conditions than in tight ion pairs, since the positive charge of the open ion is no longer stabilized electrostatically by the close counteranion, and steric strain in the cis ion **5** can result in a conversion to the trans ion **7**, or to a species of type **6b**, stabilized by some bridging interaction. Thus, under the above-specified very peculiar conditions, the product-determining step of the bromination of *cis*- and *trans*-stilbene may mainly consist of an anti collapse of the latter two intermediates, accounting for the nearly stereospecific and stereoconvergent course of these two reactions.

It is noteworthy that the previously observed changes in the steric course of the bromination of methyl *p*-methyl-*trans*-cinnamate[16] and of 2,4-hexadienes[17] in low-polarity solvents with decreasing Br_2 concentration always consisted of an increase of anti-1,2-addition. This seems therefore to be a general effect, which may be rationalized by the above discussed explanation.

Experimental Section

Materials. Commercial *cis*-stilbene (Aldrich ≥97%) and *trans*-stilbene (Schuchardt >99%) were purified before use, as previously reported.[5] Nitromethane (Merck >98%) was distilled before use.

meso- (**3**) and *d,l*-1,2-dibromo-1,2-diphenylethane (**4**) were prepared from *trans*- and *cis*-stilbene with tetrabutylammonium tribromide.[5,11]

1,2-Dichloroethane and bromine (both C. Erba RPE 99.5%) were treated as previously reported.[25]

Bromination Procedure. A 1,2-dichloroethane solution of olefin **1** or **2** (0.5 mL) was rapidly added to a Br_2 solution in the same solvent (5 mL) with vigorous stirring in a thermostated bath at 25 °C. The reagent concentrations after mixing are reported in Table I. After 3 h the reaction mixtures were washed with saturated aqueous $NaHSO_3$ and water and subjected to HPLC analysis. Checks at shorter times were also occasionally made. All reactions were carried out in triplicate. Yields were occa-

(21) The involvement of intimate or solvent-separated ion pairs in olefin bromination in low polarity solvents has been discussed: Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469, 1477.

(22) Heublein, G.; Umbreit, P. *Tetrahedron* **1968**, *24*, 4733.

(23) A referee has argued that changes in bridging with progressing ion pair dissociation are in contrast with a rate-stereochemistry correlation established for the multipathway bromination scheme of *trans*-β-methylstyrenes,[24] indicating that in methanol bridging is not modified from the rate-determining transition state to the intermediate and to the product-determining transition state. We observe, however, that (i) "For the interpretation of the structural effects the simplified scheme is sufficient if the rate-determining step is not reversible" (see ref 15a). The rate-determining step has been considered to be irreversible in methanol, but has been shown to be reversible in 1,2-dichloroethane, [5] the solvent used in the present investigation. (ii) The above-mentioned correlation is based on rate data obtained in methanol and product distributions determined in methylene chloride, assuming that no change in dibromide ratios occurs in these two solvents of very different polarity. Moreover, this correlation is stated to hold only for the very minor dibromide products (5% in the case of *trans*-β-methylstyrene, see footnote 34a in ref 24), but not for the main methoxy bromide products, which are said to be always formed stereospecifically, in spite of the fact that the two types of products arise from the same intermediate. (iii) We are suggesting equilibration between open and bridged intermediates only in solvent-separated ion pairs in low polarity solvents, i.e., under very peculiar and yet unexplored conditions.

(24) Ruasse, M.-F.; Argile, A.; Dubois, J.-E. *J. Am. Chem. Soc.* **1978**, *100*, 4645.

(25) Bellucci, G.; Berti, G.; Bianchini, R.; Ingrosso, G.; Ambrosetti, R. *J. Am. Chem. Soc.* **1980**, *102*, 7480.

sionally determined by HPLC after addition of an appropriate amount of a 1,2-dichloroethane stock solution of *erythro*-1,2-dibromo-1-phenylpropane, obtained by bromination of *trans*-1-phenylpropene with tetrabutylammonium tribromide in 1,2-dichloroethane and crystallized from chloroform, mp 63–65 °C. In complete reactions the dibromide yields amounted to 95–100%.

Several runs (3, 4, 7, and 13 of Table I) were monitored at different times during the course of the reactions by sample withdrawal and HPLC analysis.

The bromination of *trans*- and *cis*-stilbene in nitromethane was carried using a procedure identical with that described above for bromination in 1,2-dichloroethane.

The stability of dibromides **3** and **4** in the presence of Br_2 was checked by exposing both dibromides (10^{-2} to 10^{-4} M) to a 10- to 50-fold excess of Br_2 in 1,2-dichloroethane at 25 °C for 3 h, followed by HPLC analysis.

Product Analysis. The product distributions were determined by HPLC using a 25-cm Hypersil 10 C18 column (HPLC technology) and UV detector (λ 240 nm), with methanol–water (70:30 v/v) as the eluant at a flow rate of 1.5 mL/min. The reaction mixtures were directly injected after appropriate dilution. The product ratios and the yields were respectively determined by using calibration curves obtained with the pure dibromides and olefins, and the standard. The dibromides distributions reported in Table I are the averages of triplicate runs and were reproducible to ±1%.

Kinetic Measurements. Bromine solutions in 1,2-dichloroethane were prepared shortly before use and stored in the dark for no longer than 3–4 h. Their concentrations were determined from the Br_2 absorption (ϵ_{max} 211 M^{-1} cm^{-1} at λ_{max} 409 nm) and adjusted to twice the desired initial concentrations in the kinetic runs. Aliquots of these solutions were prethermostated at 25 °C (±0.05 °C) and mixed with an equal volume of prethermostated solutions of *cis*-stilbene of suitable concentration, prepared by weighing. The fastest reaction (run 1 of Table II) was carried out with a stopped-flow instrument equipped with a 2-cm observation cell, monitoring the disappearance of Br_2 at 530 nm (ϵ 34 M^{-1} cm^{-1}). Runs 2 and 3 of Table I were carried out in 4-cm cells using a conventional UV–vis spectrophotometer and monitoring the disappearance of Br_2 at 409 nm. Run 4 of Table II was followed by withdrawing from the reaction mixture samples of exactly known volume, which were treated with a saturated solution of Na_2SO_3 to reduce the excess Br_2. An appropriate amount of a 1,2-dichloroethane solution of *erythro*-1,2-dibromo-1-phenylpropane was added to each sample, and the amounts of unreacted olefins and formed dibromides were determined by HPLC under the above reported conditions. The data in runs 1 and 2, in run 3, and in run 4 of Table II were respectively fitted to the third-order, pseudo-second-order, and pseudo-first-order rate equation. In the last two cases third-order rate constants were calculated from the pseudo-second- and pseudo-first-order constants assuming an overall third-order dependence of the rate. The k_3 values are reported in Table II.

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Registry No. 1, 645-49-8; 2, 103-30-0; 3, 13440-24-9; (±)-4, 13027-48-0; *erythro*-$Ph(CH(Br))_2CH_3$, 127154-65-8; *trans*-$PhCH{=}CHCH_3$, 873-66-5; tetrabutylammonium tribromide, 38932-80-8.

Interplay between Conjugative and Steric Effects in Cyclopropylarenes

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The X-ray crystal structures of three cyclopropylarenes are reported. The data suggest that, for the series phenyl → α-naphthyl → 9-anthryl, increasing steric interactions force a distortion from the normally preferred bisected conformation to the perpendicular conformation. In the bisected conformation, orbital alignment between the aromatic π-system and the cyclopropyl HOMO is maximal and electron donation from the cyclopropyl to the arene can be detected by an asymmetry in the lengths of the vicinal and distal C–C bonds of the cyclopropane ring. In the perpendicular conformation, the π-system of the arene is orthogonal to the HOMO, but aligned with the LUMO of the cyclopropyl group. Consequently, the cyclopropyl group can only act as an electron acceptor. Within experimental error, there was no apparent asymmetry in the lengths of the vicinal and distal C–C bonds, suggesting no significant electronic interaction between the arene and the cyclopropyl group in the perpendicular conformation.

Introduction

The structure and chemistry of cyclopropane derivatives have intrigued chemists for decades. Possessing both alkanic and alkenic properties, the cyclopropyl group has found a unique niche in functional group chemistry.[1] The Walsh (Sugden) model[2] envisages that cyclopropane is "built" from three sp^2-hybridized CH_2's, with the sp^2 hybrids oriented radially toward the center of the three-membered ring and the three p orbitals coplanar (Figure 1).

When attached to a π-system, the cyclopropyl substituent is a good π-electron donor. It is well-founded, in both theory and experiment, that these π-donor properties of the cyclopropyl group are conformation-dependent. Because of the π-symmetry associated with the highest occupied molecular orbital (3e′) of the cyclopropyl group, interaction with an adjacent π-system is maximal when the orbitals are coplanar (i.e., "bisected" conformation **1**). In the alternative "perpendicular" conformation **2**, the HOMO of the cyclopropyl group is orthogonal to the π-system and the interaction is minimal.[3,4]

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