Kinetics and Mechanisms of Electrophilic Addition. II. A Thermochemical–Kinetic Approach to Transition-State Structure

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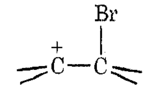
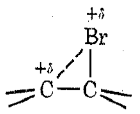
The enthalpies of isomerization (ΔH_i) of six pairs of geometrically isomeric 1,2-disubstituted ethylenes were either determined directly from heat of combustion measurements or obtained from literature values. These ΔH_i values were corrected to acetic acid conditions by measuring heats of solution in that solvent. Bimolecular rate constants (k_2) for bromination of ten of the above olefins, and several more of interest, were determined at several temperatures in acetic acid using stopped flow methods in most cases. Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained for each isomer. These reactions were also analyzed for dibromide–acetoxybromide product distribution and product stereochemistry. In some cases stereospecific anti addition was observed, and in others variable stereoselectivity was obtained. However, in all cases the initial enthalpy difference between starting cis and trans isomers was increased at the bromination transition state. It is concluded that, although bridged transition states are involved in all cases, these may lead to either bridged or open cationic intermediates, depending on the nature of the attached groups. It is also shown that in these reactions large values of $\Delta\Delta H$ and $\Delta\Delta F$ (cis–trans) for the reactants do not generally decrease monotonically along the reaction coordinate as small $\Delta\Delta H$ and $\Delta\Delta F$ values for the diastereomeric products are approached.

For a long time, electrophilic bromine additions to olefins were considered to be generally stereospecific and anti, which was explained in terms of the well-known cyclic bromonium ion intermediate of Roberts and Kimball,[1] but it is now clear that these reactions can show variable stereoselectivity, ranging all the way from predominant syn to exclusive anti addition.[2] The nature of the intermediate has been shown to depend strongly on starting olefin structure and on the solvent, and it is now more reasonable to propose a spectrum of possible ionic intermediates, of which I and III are extremes.



I
(free rotation)



II
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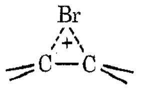

III
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It has proved difficult to obtain unequivocal evidence about the structures of these cationic intermediates, and more particularly about the transition states which precede and presumably closely resemble them. Stereochemical studies give information only about the structure of the product determining intermediates. Similarly kinetic studies give information only about the charge distribution in the preceding transition states. We have therefore been interested in developing alternative methods of assessing the importance of bromonium ion structures, both as intermediates and as transition states, and have reported[3] some preliminary results using a combined thermochemical–kinetic product study approach.

The approach is based on a comparison of the reactions of pairs of cis- and trans-disubstituted ethylenes. In comparing such systems the considerable difference in steric interactions between the groups R is reflected in the heats of combustion of the isomers. The cis group interactions result in values of ΔH_c for the cis isomers which are higher than those for the trans by ~1–10 kcal for typical olefins.[4] It is therefore of interest to try to determine to what extent these steric differences are retained at the transition states for electrophilic addition. If the transition state resembles I, the steric repulsions in the cis case would be relieved by a combination of bond length and hybridization changes (see Appendix) and could also be further relieved by a small rotation of the C–C bond, thus significantly reducing the ground-state enthalpy difference between cis and trans olefin.[5]

If the transition state resembles III, then this difference in steric repulsions would either be retained or more probably accentuated (see Appendix) as the groups R are forced together owing to a combination of bond length and hybridization changes. Thus the initial isomeric enthalpy difference would be maintained or increased at the transition state.

Therefore, by appropriately combining ΔH_c values for pairs of geometrical isomers with values of $\Delta H^\ddagger$ for bromination it should be possible to determine to what extent the transition state geometry resembles the extremes I or III, for different types of olefinic substrates.

Results and Discussion

Choice of Substrates.—The pairs of olefins studied were all 1,2-disubstituted ethylenes, chosen to span a wide range of bromination reactivity and of ground-state stability difference. Several highly reactive 1,2-dialkylethylenes (diisopropyl, *tert*-butylethyl and di-*tert*-butyl) were used as model substrates of the type expected to lead to cyclic bromonium ion intermediates.[7] The cyclooctenes were investigated to determine whether the severe ring distortion which destabilizes the trans relative to the cis isomer would cause this pair to behave differently from "normal"

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[1] I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937).

[2] See, for example, R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962); R. E. Fahey and C. Shubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965); J. H. Rolston and K. Yates, *ibid.*, **91**, 1469, 1477, 1483 (1969).

[3] K. Yates and R. S. McDonald, *J. Amer. Chem. Soc.*, **93**, 6297 (1971).

[4] H. F. Bartolo and F. D. Rossini, *J. Phys. Chem.*, **64**, 1685 (1960), and references therein.

[5] There is already evidence that this can occur for type I transition states, based on the acid-catalyzed hydrations of *cis*- and *trans*-stilbenes.[6] In this case, the rate-determining step is proton transfer to give an open carbonium ion. An initial ground-state difference of 5.7 kcal between the two isomers was found to decrease to only 2.7 kcal at the transition state.

[6] D. R. Hartter, Ph.D. Dissertation, University of California, Berkeley, 1964.

[7] Alkyl-substituted ethylenes are known to give essentially 100% stereospecific anti addition of bromine and yield virtually no solvent-incorporated products in solvents such as acetic acid.[2]

TABLE I

ENTHALPY OF COMBUSTION, ENTHALPY OF FORMATION, AND ENTHALPY OF ISOMERIZATION ON ISOMERIC PAIRS

Compound[a]	No. of runs	$-\Delta E_c°$ [b,c]	$-\Delta H_c°$ [c,d]	$-\Delta H_f°$ [c,e]	$-\Delta H_i$ [f,g]
trans-Diisopropylethylene	5	1258.50 ± 0.35	1260.87 ± 0.35	38.07 ± 0.35	−1.96 ± 0.30
cis-Diisopropylethylene	6	1260.47 ± 0.44	1262.83 ± 0.44	36.11 ± 0.44	
trans-tert-Butylethylethylene	6	1258.85 ± 0.48	1261.22 ± 0.48	37.72 ± 0.48	−5.12 ± 0.38
cis-tert-Butylethylethylene	6	1263.96 ± 0.37	1266.34 ± 0.37	32.60 ± 0.37	
trans-β-tert-Butylstyrene	3	1667.37 ± 0.99	1669.74 ± 0.99	5.40 ± 0.99	−7.79 ± 0.92
cis-β-tert-Butylstyrene	3	1675.16 ± 0.50	1667.53 ± 0.50	−2.39 ± 0.50	

[a] Registry numbers are, respectively, 692-70-6, 10557-44-5, 690-93-7, 690-92-6, 3846-66-0, 3740-05-4. [b] Standard heat of combustion in kcal/mol. [c] Errors quoted are standard deviations of the mean and include uncertainty in calorimeter calibration value. [d] Standard enthalpy of combustion in kcal/mol. [e] Standard enthalpy of formation in kcal/mol. [f] Enthalpy of isomerization in kcal/mol [$\Delta H_f°$(trans) − $\Delta H_f°$(cis)]. [g] Errors quoted are standard deviations of the difference and do not include calorimeter calibration uncertainty.

1,2-dialkylethylenes. A number of phenyl-substituted systems were also studied. The stilbenes were chosen since the cis isomer is known to give nonstereospecific addition in acetic acid.[8] Thus, this isomer at least must form an open ion intermediate before the product-determining step. The β-methylstyrenes are known to react *via* open or only very weakly bridged ions.[9] To destabilize the cis isomer further relative to the trans, the β-*tert*-butylstyrenes were also investigated as being good models for substrates producing open ion intermediates.

Heats of Combustion.—The heats of combustion of each isomer of three pairs of 1,2-disubstituted olefins were carefully and repeatedly determined using an adiabatic bomb calorimeter and are reported in Table I. These data were used to obtain values of the standard enthalpies of combustion ($\Delta H_c°$) and formation ($\Delta H_f°$) of the olefins, which are also listed in Table I. All values refer to the idealized process at 1.0 atm and 25°. Values of the enthalpies of isomerization, $\Delta H = [\Delta H_f°(\text{trans}) - \Delta H_f°(\text{cis})]$ are collected in Table II, along with values obtained from literature data on heats of combustion or hydrogenation for a number of other isomeric olefins of interest.[10–17] With one exception there is good agreement between ΔH_i values based on combustion and hydrogenation. There is some conflict between the reported values for the enthalpy (and free energy) difference between *cis*- and *trans*-stilbene. Thermal isomerization of the trans isomer to give an equilibrium mixture yielded a ΔG_i value of −3.0 kcal/mol at 330°.[18] A study of the iodine-catalyzed isomerization of stilbenes and measurement of the equilibrium constant as a function of temperature gave ΔG_i and ΔH_i values of −3.7 and −2.9 kcal/mol, respectively, in methylcyclohexane at 27°.[19] The enthalpy difference between the solid trans isomer and the liquid cis isomer is −12.85 kcal/mol from hydrogenation measurements[15] and −10.29 kcal/mol from combustion results.[14] When corrected for the heat of fusion of the trans isomer (7.19 kcal/mol),[17] the ΔH_i values for the pure liquids listed in Table II are obtained. The discrepancy between the hydrogenation value and the other results will be discussed later.

TABLE II

COLLECTED VALUES OF ENTHALPY OF ISOMERIZATION FOR CIS- AND TRANS-1,2-DISUBSTITUTED ETHYLENES

1,2 substituents[a]	ΔH_i, kcal mol^{-1} [b] $\Delta\Delta H_c$ [c]	Ref	$\Delta\Delta H_h$ [d]	Ref
Methyl, methyl*	−0.75[e]	10	−0.95[e]	11
Methyl, *n*-propyl*	−0.39	4		
Methyl, isopropyl*	−1.08	4	−0.94	12
Ethyl, ethyl*	−1.70	4		
Methyl, *tert*-butyl*	−3.92	13	−4.29	12
Ethyl, *tert*-butyl	−5.12			
Isopropyl, isopropyl	−1.96			
tert-Butyl, *tert*-butyl*	−10.51		−9.37	12
tert-Butyl, phenyl	−7.79			
Phenyl, phenyl*	−3.10[f]	14	−5.66[f]	15
Cyclooctene*			+9.26	16
Cyclononene*			+2.87	16
Cyclodecene*			+3.34	16

[a] Registry numbers pertaining to asterisked entries, cis (trans), are, respectively, 590-18-1 (624-64-6), 7688-21-3 (4050-45-7), 691-38-3 (674-76-0), 7642-09-3 (13269-52-8), 762-63-0 (690-08-4), 692-47-7 (692-48-8), 645-49-8 (103-30-0), 931-87-3 (931-89-5), 933-21-1 (3958-38-1), 935-31-9 (2198-20-1). [b] The enthalpies of isomerization refer to the process cis olefin → trans olefin with both isomers in the liquid phase at 25°, unless otherwise noted. [c] Derived from enthalpies of combustion [ΔH_c(trans) − ΔH_c(cis)]. [d] Derived from enthalpies of hydrogenation [ΔH_h(trans) − ΔH_h(cis)]. [e] ΔH_i values refer to the gas phase. [f] Corrected for the latent heat of fusion of the trans isomer, 7.19 kcal/mol.[17]

It can be seen from the ΔH_i values in Table II that for simple olefins the cis isomer is significantly destabilized (by up to 10.5 kcal) with respect to the trans in every case (except the cyclic olefins). This is particularly notable when one or more of the adjacent groups is *tert*-butyl. It should therefore be easy to detect what happens to these large steric differences, as the bromination transition states are approached, by measuring $\Delta H^{\ddagger}$ values for each isomer, and thus obtain information about their structures.

Although ideally comparisons should be made on both an enthalpy and free-energy basis, entropy of isomeriza-

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(8) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962).

(9) These olefins give nonstereospecific bromine addition in acetic acid and significant yields of solvent-incorporated products, which are formed completely regiospecifically in the Markovnikov sense.[2]

(10) E. J. Prosen, F. W. Mason, and F. D. Rossini, *Nat. Bur. Stand. J. Res.*, **46**, 106 (1951).

(11) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **57**, 876 (1935).

(12) R. B. Turner, D. E. Nettleton, and M. Perelman, *J. Amer. Chem. Soc.*, **80**, 1430 (1958).

(13) J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, **65**, 267 (1961).

(14) J. Coops and G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **69**, 538 (1950).

(15) R. B. Williams, *J. Amer. Chem. Soc.*, **64**, 1395 (1942).

(16) R. B. Turner and W. R. Meadar, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).

(17) International Critical Tables, Vol. V, National Research Council, E. W. Washburn, Ed., McGraw-Hill, New York, N. Y., p 134.

(18) G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, **56**, 368 (1934).

(19) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc.*, **94**, 4580 (1972), and references cited therein.

TABLE III

HEATS OF SOLUTION AND ENTHALPIES OF ISOMERIZATION IN ACETIC ACID[a]

Compound	ΔE_{soln}[b]	$\Delta\Delta H_{soln}°(\infty)$[c]	ΔH_i[d]	ΔH_i (soln)[e]
trans-Diisopropylethylene	0.71	−0.04 ± 0.02[f]	−1.96 ± 0.30[g]	−2.00
cis-Diisopropylethylene	0.75			
trans-tert-Butylethylethylene	1.01 ± 0.05	+0.20 ± 0.03	−5.12 ± 0.38[g]	−4.92
cis-tert-Butylethylethylene	0.81 ± 0.04			
trans-Di-*tert*-butylethylene	1.42 ± 0.09	+0.31 ± 0.05	−10.51 ± 0.36	−10.20
cis-Di-*tert*-butylethylene	1.11 ± 0.06			
trans-β-Methylstyrene	0.36 ± 0.02	−0.02 ± 0.02		
cis-β-Methylstyrene	0.38 ± 0.02			
trans-β-*tert*-Butylstyrene		+0.20[h]	−7.79 ± 0.92[g]	−7.6
cis-β-*tert*-Butylstyrene				
trans-Stilbene	5.89 ± 0.30	+5.26 ± 0.30	−10.29 ± 0.22	−5.03
cis-Stilbene	0.63 ± 0.04			

[a] All values given in kcal mol^{-1}. [b] The observed heat of solution (ΔE_{soln}) is assumed to be identical with the standard enthalpy of solution at infinite dilution [$\Delta H_{soln}°(\infty)$]. The errors quoted include the assumed uncertainty in the heat of solution of the reference compound (see Experimental Section for details). [c] $\Delta\Delta H_{soln}°(\infty) = \Delta H_{soln}°(\infty)(\text{trans}) - \Delta H_{soln}°(\infty)(\text{cis})$. The errors quoted are standard deviations of the difference. [d] The enthalpy of isomerization for the neat compounds at 25.0. Values are all derived from combustion data. References to literature data are given in Table VI. The error quoted is the standard deviation of the difference [$\Delta H_f°(\text{trans}) - \Delta H_f°(\text{cis})$]. [e] The enthalpy of isomerization in acetic acid solution at 25.0° [$\Delta H_i(\text{soln}) = \Delta H_i + \Delta\Delta H_{soln}°(\infty)$]. [f] Estimated error. [g] This work. [h] This value is estimated (see text).

tion (ΔS_i) values are not easy to obtain from nonequilibrium measurements.[20] The instrumental techniques required for the extensive heat capacity (C_p) measurements from 0–298°K were not available; so it was decided to make comparisons on a purely enthalpic basis. It is known, however, that the ΔS_i values of cis–trans isomeric olefins are very small, in general, in the range of −1 to −2 cal/deg mol[21] (corresponding to a ΔG_i contribution of $\leq$0.6 kcal/mol at 25°). Although this normally tends to reduce (make less negative) the ΔG_i difference from that reflected by the ΔH_i values (the trans isomer has a lower standard entropy than the cis), the trans isomer will be more stable than the cis on both an enthalpy and free-energy basis.

Heats of Solution.—Since all kinetic work was carried out in acetic acid, differences in activation parameters therefore refer to that solution. Thus, ground-state enthalpy values (or differences) in the previous section may need to be adjusted for heats of solution of the olefins in acetic acid. Heats of solution of selected olefins were measured in acetic acid. The heats of solution (ΔE_{soln}), assumed to be identical (see Experimental Section) with the enthalpies of solution at infinite dilution [$\Delta H_{soln}(\infty)$], of five olefin pairs are collected in Table III. The $\Delta\Delta H_{soln}$ values required to correct the enthalpies of isomerization of the neat substrates to acetic acid solution are also given in Table III.

The β-methylstyrenes were chosen as models for the β-*tert*-butylstyrenes since only limited quantities of the latter compounds were available. The cis and trans isomers of the β-methylstyrenes and the diisopropylethylenes have essentially identical ΔH_{soln} values. In fact, only where the ground-state enthalpy differences become fairly large (where one of the ethylene substituents is a *tert*-butyl group) do the $\Delta\Delta_{soln}$ values become appreciable. (The difference is large in the case of the stilbenes only because the trans isomer is dissolved as a solid.) A prediction may be made of the $\Delta\Delta H_{soln}$ for the β-*tert*-butylstyrenes from these results. Since the β-methylstyrenes have a $\Delta\Delta H_{soln}$ value of essentially zero, and, since it appears that a *tert*-butyl substituent interacting with a non-*tert*-butyl substituent leads to $\Delta\Delta H_{soln}$ value of $\simeq$0.2 kcal/mol, then a $\Delta\Delta H_{soln}$ value for the β-*tert*-butylstyrenes may be assumed to be roughly 0.2 kcal/mol.

From the $\Delta\Delta H_{soln}$ values of the other isomeric pairs, it would be expected that the heats of solution of the stilbenes, if both were in the liquid phase, would be the same to within a few tenths of a kilocalorie. However, in order that our heat of solution data be compatible with the only available value[17] for the heat of fusion of the trans isomer (7.19 kcal/mol), the heat of solution of liquid *trans*-stilbene would have to be roughly −1.3 kcal/mol. Such a fairly large, negative ΔE_{soln} would be totally unexpected since all the other olefins have positive values. This suggests that the very old heat of fusion value is probably in error by 1–2 kcal/mol.

As mentioned previously there is a serious discrepancy between the value of ΔH_i for stilbenes based on hydrogenation data and those based on other approaches, including heats of combustion. Also, the hydrogenation work[15] involved use of *cis*-stilbene of questionable purity. Since our heat of solution results do take into consideration that the trans isomer is dissolved as a solid, correcting the combustion values to acetic acid solution leads to a ΔH_i(soln) value of −5.03 kcal/mol, which is free of the above uncertainty in the reported heat of fusion value. Further, if it is assumed that the ΔH_i(soln) of the β-*tert*-butylstyrenes ($\simeq$−7.6 kcal/mol) is roughly midway between that for the stilbenes and the di-*tert*-butylethylenes (−10.2 kcal mol^{-1}), as seems reasonable, the ΔH_i(soln) for the stilbenes should be roughly −5 kcal. This is very close to the value obtained by correcting the combustion data to acetic acid conditions and suggests that the combustion results are the more reliable. These will be used wherever possible for comparisons of isomeric olefins. The enthalpies of isomerization in acetic acid for the isomeric

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[20] The choice of olefins in this study precludes the use of equilibrium measurements, since only one of the olefin pairs of interest has an enthalpy (and probably free energy) difference less negative than −4 kcal/mol. A ΔG_i of −4.1 kcal/mol between a pair of cis–trans olefins corresponds to an equilibrium constant of 10^3. Thus, a method of analyzing accurately for 0.1% or less of the cis olefin in the presence of 99.9% or more of the trans would be required.

[21] H. Akimoto, J. L. Sprung, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **94**, 4850 (1972), and references cited therein.

olefins of principal interest in the present study are listed in Table III.

Bromination Rates.—Of the six olefin pairs originally chosen for a complete kinetic study, work on one pair (the cyclooctenes) was discontinued since the trans isomer reacted too rapidly to be followed even by the stopped-flow technique. The bimolecular rate constants (k_2) for the other five olefinic pairs were measured at a series of temperatures by either stopped-flow or conventional spectrophotometric methods, as described in the Experimental Section. The bimolecular rate constants determined for these five olefin pairs and for several other olefins of interest are collected in Table IV. It can be seen that the 1,2-dialkylethylenes react very rapidly with bromine in acetic acid with rate constants (k_2) in the range of 10^2–10^3 M^{-1} sec^{-1}. Styrenes react less rapidly, but are still very reactive (with k_2 in the range of 10^2–10^{-1} m^{-1} sec^{-1}). The stilbenes are much less reactive ($k_2 \sim 10^{-1}$–10^{-2} M^{-1} sec^{-1}). These rate differences are qualitatively explicable in terms of the electrophilic nature of the additions and the combined inductive and conjugative effects of the substituent groups on both the olefin and its transition state.

TABLE IV

BIMOLECULAR RATE CONSTANTS (k_2) FOR THE BROMINATION OF SOME 1,2-DISUBSTITUTED OLEFINS IN ANHYDROUS ACETIC ACID

Compound	No. of runs	t, °C	k_2,[a] M^{-1} sec^{-1}
cis-Diisopropylethylene	2	17.8	$(2.08 \pm 0.07) \times 10^2$
	3	25.0	2.68 ± 0.08
	2	32.2	4.56 ± 0.13
	2	38.4	5.36 ± 0.35
	2	44.3	5.87 ± 0.30
	2	45.2	6.19 ± 0.28
trans-Diisopropylethylene	2	18.0	$(4.80 \pm 0.30) \times 10^2$
	2	25.0	6.37 ± 0.27
	2	32.1	7.79 ± 0.56
	2	38.3	10.04 ± 0.35
	3	44.5	12.53 ± 0.10
cis-*tert*-Butylethylethylene	3	18.4	$(7.28 \pm 0.35) \times 10^2$
	2	25.0	11.17 ± 0.07
	2	32.1	11.76 ± 0.57
	2	38.3	16.53 ± 0.37
	2	44.4	21.08 ± 0.22
trans-*tert*-Butylethylethylene	2	17.9	$(3.31 \pm 0.12) \times 10^2$
	2	25.0	4.47 ± 0.08
	3	32.2	6.47 ± 0.21
	2	38.4	7.91 ± 0.48
	4	44.5	9.12 ± 0.09
cis-Di-*tert*-butylethylene	2	20.0	$(4.58 \pm 0.15) \times 10^2$
	2	25.0	5.29 ± 0.07
	2	32.0	7.59 ± 0.06
	2	38.0	9.72 ± 0.20
trans-Di-*tert*-butylethylene	2	20.0	8.18 ± 0.10
	2	25.0	11.4 ± 0.3
	3	32.1	12.2 ± 0.4
	3	38.0	14.4 ± 0.5
cis-Stilbene	3	25.1	$(5.44 \pm 0.10) \times 10^{-2}$
	2	30.3	7.45 ± 0.09
	4	35.2	10.87 ± 0.44
	2	43.1	19.78 ± 0.35
trans-Stilbene	2	25.1	$(1.84 \pm 0.04) \times 10^{-2}$
	3	30.4	2.62 ± 0.11
	2	35.2	3.40 ± 0.04
	4	43.2	6.43 ± 0.24
cis-β-*tert*-Butylstyrene	2	25.0	2.97 ± 0.08
	2	32.0	3.70 ± 0.12
	2	38.0	4.37 ± 0.11
	2	45.2	5.18 ± 0.42
trans-β-*tert*-Butylstyrene	2	20.0	18.4 ± 0.6
	2	25.0	19.6 ± 0.9
	3	32.1	20.7 ± 1.6
	2	38.0	22.8 ± 0.7
cis-Cyclooctene	2	25.0	$(8.42 \pm 0.18) \times 10^2$
trans-Cyclooctene		25.0	$\geq 5 \times 10^5$ [b]
cis-2-Butene	3	25.1	$(11.62 \pm 0.42) \times 10^2$
trans-2-Butene	2	25.1	$(9.23 \pm 0.43) \times 10^2$
cis-3-Hexene	2	25.0	$(21.7 \pm 1.3) \times 10^2$
trans-3-Hexene	2	25.0	$(19.6 \pm 0.8) \times 10^2$
1-Hexene	4	25.1	31.8 ± 2.1

[a] The errors quoted are standard deviations. [b] This compound reacted too rapidly to be followed by stopped flow. The number quoted is a lower limit for the rate constant.

Apart from two pairs of olefins in Table IV, the cis:trans rate ratios fall in the range of 0.15–3, as shown in Table V. These small rate ratios correspond to differences in free energy of activation ($\Delta\Delta G^{\ddagger}$) in the range of -1 to $+1$ kcal/mol. It has been previously assumed that the often observed fact that a cis olefin reacts more rapidly than its trans isomer (indicative of a closing of the free-energy gap between the starting olefin pair, since ΔG_i is usually <0), is caused by relief of steric strain in the cis olefin in going from the ground state to the transition state. In fact for three of the nine isomeric pairs listed in Table V, this free-energy difference actually increases (the ΔG_i gap becomes more negative). Thus it is dangerous to draw much mechanistic conclusions from these generally small and variable rate ratios (or free-energy differences) which are in any case composites of enthalpy and entropy contributions.[22]

TABLE V

CIS:TRANS RATE CONSTANT RATIOS AND CORRESPONDING DIFFERENCES IN FREE ENERGY OF ACTIVATION FOR THE BROMINATION OF ISOMERIC OLEFIN PAIRS

Isomeric pair	k_c/k_t	$\Delta\Delta G^{\ddagger}$,[a] kcal/mol	Effect on isomeric ΔG difference at transition state
2-Butenes	1.26	$+0.14$	Decrease
3-Hexenes	1.11	$+0.06$	Decrease
Diisopropylethylenes	0.42	-0.51	Increase
tert-Butylethylethylenes	2.35	$+0.51$	Decrease
Di-*tert*-Butylethylenes	51.9	$+2.34$	Decrease
Cyclooctenes	<0.002	<-3.7[b]	Decrease
Stilbenes	2.96	$+0.64$	Decrease
β-Methylstyrenes[c]	0.72	-0.19	Increase
β-*tert*-Butylstyrenes	0.15	-0.12	Increase

[a] $\Delta\Delta G^{\ddagger}[\Delta G^{\ddagger}(\text{trans}) - \Delta G^{\ddagger}(\text{cis})] = RT \ln k_c/k_t$. A negative $\Delta\Delta G^{\ddagger}$ value shows that the isomeric free energy difference (ΔG_i) is accentuated at the transition state (one exception is the cyclooctene case; see *b*). [b] In this case, the ground state ΔG_i is positive (the cis isomer is more stable than the trans) and the negative $\Delta\Delta G^{\ddagger}$ value implies that the free-energy gap is closing at the transition state. [c] From ref 2.

In addition the large steric differences between cis and trans isomers are reflected mainly in the enthalpy terms (ΔH_i). It is therefore of more interest to examine the individual activation parameters $\Delta H^{\ddagger}$

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[22] Since steric differences between cis and trans olefins can be as high as 10 kcal, it is evident from the small rate ratios in Table VI that relief of steric strain can not be an important factor in these reactions, even where $k_c/k_t > 1$.

TABLE VI

ENTHALPY AND ENTROPY OF ACTIVATION TERMS FOR BROMINATION OF ISOMERIC OLEFIN PAIRS[a]

Isomeric pair	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol	$\Delta\Delta H^{\ddagger}$,[b] kcal/mol	$-T\Delta\Delta S^{\ddagger}$,[b,c] kcal/mol	$\Delta\Delta G^{\ddagger}$,[b,c,d] kcal/mol
cis-Diisopropylethylene	6.96 ± 0.53	−23.9 ± 1.7	−0.96 ± 0.60	+0.51 ± 0.57	−0.45
trans-Diisopropylethylene	6.00 ± 0.28	−25.6 ± 0.9			
cis-*tert*-Butylethylethylene	6.56 ± 0.53	−22.9 ± 1.8	−0.29 ± 0.62	+0.72 ± 0.63	0.43
trans-*tert*-Butylethylethylene	6.27 ± 0.32	−23.0 ± 1.0			
cis-Di-*tert*-butylethylene	6.83 ± 0.29	−23.0 ± 1.0	−2.38 ± 0.67	+4.77 ± 0.66	+2.39
trans-Di-*tert*-butylethylene	4.45 ± 0.60	−39.0 ± 2.0			
cis-Stilbene	12.78 ± 0.45	−21.5 ± 1.5	−0.29 ± 0.67	+0.78 ± 0.66	+0.49
trans-Stilbene	12.49 ± 0.49	−24.1 ± 1.6			
cis-β-*tert*-Butylstyrene	4.58 ± 0.50	−41.0 ± 1.6	−3.19 ± 0.77	+2.09 ± 0.75	−1.10
trans-β-*tert*-Butylstyrene	1.39 ± 0.58	−48.0 ± 1.9			

[a] Errors quoted are standard deviations, or standard deviations of the difference (for the ΔΔ quantities). [b] $\Delta\Delta X^{\ddagger}$ refers to the difference $\Delta X^{\ddagger}$(trans) − $\Delta X^{\ddagger}$(cis). [c] At 25.0°. [d] $\Delta\Delta G^{\ddagger} = \Delta\Delta H^{\ddagger} - T\Delta\Delta S^{\ddagger}$ at 25.0°.

and $\Delta S^{\ddagger}$ in attempting to obtain mechanistic information.

Activation Parameters.—The enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation for five olefin pairs were calculated from correlations of log k_2/T *vs.* $1/T$ using the rate data in Table IV. These values are given in Table VI along with the differences [$\Delta X^{\ddagger}$(trans) − $\Delta X^{\ddagger}$(*cis*)] in these values and their relative contributions to the total difference in free energy of activation.[23]

The most striking observation on separating the enthalpy–entropy contributions is that, regardless of the direction or magnitude of the isomeric difference in free energy of activation, all of the enthalpy differences are negative and all of the corresponding entropy contributions are positive. For all of these pairs, ΔG_i is negative (the trans isomer is thermodynamically more stable than the cis isomer). Thus, while three of the pairs, the stilbenes and the *tert*-butylethyl- and di-*tert*-butylethylenes, tend to lower this free-energy difference, the other two pairs tend to increase the ΔG_i gap, at the bromination transition state. However, for all of the pairs, the entropy of activation of the cis isomer is always less negative than that for the trans compound. In each case the entropy difference has a compensating effect (positive contribution to the $\Delta\Delta G^{\ddagger}$ value, as in column 4, Table VI). In terms of rates, the enthalpy term favors the trans isomer to react *more* rapidly in every case, but its entropy term is more negative and thus less favorable, which in some cases results in a lower rate for this isomer.

The enthalpy effects arise primarily from a combination of bond-making and bond-breaking effects which occur in the activated complex. However, in the absence of steric effects these should be very similar for a cis–trans olefin pair. Thus any observed enthalpy effects can be interpreted mechanistically in terms of the initial premise concerning various transition state structures and their steric effects.

Transition-State Geometry and Product Stereo-Chemistry.—The prediction that olefin pairs which proceed *via* bromonium ion type transition states should show a widening of the enthalpy gap in going from the ground to the bromination transition state is borne out here in the observed enthalpy effects [in each case, $\Delta H^{\ddagger}$(cis) > $\Delta H^{\ddagger}$(trans)]. This must mean, at least, that no rotation is occurring at the transition states and that the isomeric enthalpy gap is being increased by more severe steric interactions in the cis transition state. This is consistent with a bridged transition state leading to some type of cyclic bromonium ion intermediate. However, very surprisingly, this occurs for all pairs of substrates studied, even the β-*tert*-butylstyrenes and stilbenes. Although the enthalpy changes at the transition state are small where the initial enthalpy differences of the olefins are also small (*i.e.*, where ΔH_i is less negative than −5 kcal/mol), the $\Delta\Delta H^{\ddagger}$ is large (−2.38 kcal) for the di-*tert*-butylethylenes where ΔH_i is −7.8 kcal. The fact that in all five cases the enthalpy (or entropy) effects occur in a similar direction supports the idea that these changes, even when small, are real.

i. **Dialkylethylenes.**—The original postulate concerning the intermediacy of the bromonium ion[1] arose through studies of the stereochemistry of the olefin bromination products. The products of bromination of the cis–trans olefin pairs determined in this study and of two pairs from the literature are summarized in Table VII. In general, it is observed that the 1,2-dialkylethylenes give essentially 100% anti addition, indicative of a bridged intermediate in all of these cases. In fact the four cis isomers of this type give completely stereospecific anti-addition products. These isomers would be expected to allow rotation to relieve the ground-state steric effects and lead to nonstereospecific products, if open-ion intermediates were involved. In general, only anti-addition products are observed from the trans alkenes as well, but some unidentified product is observed in bromination of *trans*-diisopropylethylene and *trans*-di-*tert*-butylethylene. These are not, however, the products of syn addition and are probably addition–elimination products or products of the further bromination of these compounds (see Experimental Section). *trans*-Di-*tert*-butylethylene is anomalous in its behavior. Although no products of syn addition are observed, very little meso dibromide is formed. The predominant product is a rearranged bromo olefin or products from the secondary bromination of this compound. However, this olefin appears to be formed *via* a stereospecific methyl shift to a bromonium ion centre analogous to reported chlorination results.[24] The transition state for both the *cis*- and *trans*-di-*tert*-butylethylene is pro-

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(23) The $\Delta\Delta G^{\ddagger}$ values in Table VI are slightly different from those in Table V which were calculated directly from the rate constant ratios at 25°, but the differences are negligible (≤0.15 kcal).

(24) R. C. Fahey, *J. Amer. Chem. Soc.*, **88**, 4681 (1966).

TABLE VII

SUMMARY OF PRODUCTS FROM THE BROMINATION OF SOME OLEFIN PAIRS IN ACETIC ACID AT 25°[a]

Compound	Dibromides, %		Acetoxybromides, %			
	Meso or erythro	*dl* or threo	Erythro	Threo	Other[b]	Anti addition, %[c]
cis-2-Butene[d]		98		2		99.5
trans-2-Butene[d]	98		2	*h*		99.5
cis-Diisopropylethylene		>99[e]				≥99
trans-Diisopropylethylene	83[f]		~4[g]		13	≥99
cis-*tert*-Butylethylene		92[j]	*k*	8		>99
trans-*tert*-Butylethylethylene	>99[i]			*l*		>99
cis-Di-*tert*-butylethylene		>99[m]		*n*		>99
trans-Di-*tert*-Butylethylene	≤5				~95	(>99)[u]
cis-Cyclooctene		~90[o,v]	~2–3		~7	
trans-Cyclooctene		~20[v]	Total ~5		~75	
cis-Stilbene	Predominant	Present	Present	Present		<50
trans-Stilbene	>95[p]		Present			>95
cis-β-Methylstyrene[d]	22	59		20		79
trans-β-Methylstyrene[d]	64	13	23			87
cis-β-*tert*-Butylstyrene	55[q]	25[r]	18[s]	2[t]		27
trans-β-*tert*-Butylstyrene	75	23	2			77

[a] A blank indicates that none of this compound is detectable (≤0.5%). [b] Includes bromo olefin or its secondary reaction products and unidentified material (see Experimental Section for details). [c] Based on dibromide and acetoxybromide products only. [d] From ref 2. [e–t] Registry numbers. [e] 40084-92-2. [f] 40084-93-3. [g] 40084-94-4. [h] 40084-95-5. [i] 40084-96-6. [j] 40084-97-7. [k] 40084-98-8. [l] 40084-99-9. [m] 40085-00-5. [n] 40085-01-6. [o] 34969-65-8. [p] 13440-24-9. [q] 40085-04-4. [r] 40085-05-0. [s] 40085-06-1. [t] 40037-04-5. [u] No syn addition is observed in this case, but only ~15% of the total product mixture was identified. [v] This compound is the *trans*-1,2-dibromocyclooctane from an anti addition to the cis isomer or from a net syn addition to the trans isomer.

posed to resemble that for the other dialkylethylenes. However, special conformational effects must be occurring at the transition state for the trans olefin. While the trans isomer reacts 50-fold more slowly than the cis isomer, this is reflected not in the enthalpy term which actually favors the trans isomer by 2.4 kcal/mol, but in the entropy term which is unfavorable by 4.8 kcal/mol. The difference in $\Delta S^{\ddagger}$ of 16 cal/deg mol between the cis and trans isomers cannot be simply explained in terms of differences in solvation of the corresponding transition states.[25] The cis isomer behaves normally with respect to its bromination rate, activation parameters, and product stereochemistry.

Thus the thermochemical-kinetic and stereochemical studies presented here point strongly toward a bromonium ion type transition state leading to a bridged ion intermediate for the acyclic 1,2-dialkylethylenes.

ii. **Stilbenes.**—The previous compounds, adopted as models which are believed to brominate through cyclic bromonium ion intermediates, showed enthalpy effects which were interpretable in terms of a transition state leading to such an ion. However, the stilbenes also show similar effects. This is surprising, since in these cases an open ion could be resonance stabilized by one of the phenyl groups. Thus, the enthalpy gap between the isomers is found to increase by 0.29 kcal/mol and the trans isomer is found to have a $\Delta S^{\ddagger}$ value 2.6 cal/deg mol less than that of the cis isomer. These values are, in fact, very similar to those observed for the *tert*-butylethylethylene pair (which has a similar ΔH_i value) and point toward a bromonium ion type transition state for the stilbene also. However, referring to Table VII stereospecific anti addition is observed only for the trans isomer. The cis isomer gives stereoselective syn addition and isomerizes in the presence of bromine. Nonstereospecific bromine addition to stilbenes has also been reported previously.[8] An open-ion intermediate is required to explain these results, but, at the transition state leading to this ion, no rotation to relieve the steric interaction between the cis substituents is allowed. Thus, the neighboring substituent interaction actually increases slightly.

What the kinetic and stereochemical studies then imply is that both stilbenes react *via* initial formation of an essentially symmetrical charge-transfer complex with little, if any, change in steric effects in the cis olefin. Both then proceed *via* a rate-determining transition state, either with unassisted or solvent-assisted bromine–bromine bond cleavage, in which the interacting substituents in the cis olefin are forced slightly together and in which no rotation to relieve this interaction is allowed. In the case of the trans olefin, this activated complex may lead to a bromonium ion which reacts further to give products. The complex from the cis olefin probably proceeds to the formation of an open or weakly bridged ion. Thus, an unsymmetrically bridged transition state (type II) can be envisaged for these olefins. In nonpolar solvents, the unsymmetrically bridged ion does not open and only anti addition is observed.[8,26] In solvents capable of stabilizing a carbonium ion center by solvation, bridging is sufficiently weakened to allow C_α–C_β bond rotation, resulting in nonstereospecific addition. Since the relative rate of bromine addition to *cis*-stilbene and its rate of bromine-catalyzed isomerization are not known, the question arises as to what extent nonstereospecific addition is due to collapse of this open

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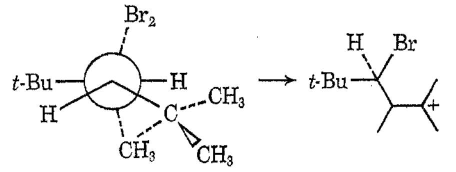
[25] A referee has suggested that this large difference may point to a quite different transition state for *trans*-di-*tert*-butylethylene, because the incoming bromine cannot avoid the bulky groups by attacking off the perpendicular,



as it could in the cis isomer. This could lead directly to a different intermediate and the observed rearranged product.

[26] G. Heublein, *J. Prakt. Chem.*, **31**, 84 (1966).

ion with bromide (leading predominantly to meso dibromide) or to prior isomerization to the trans olefin which is known to brominate anti to give the meso dibromide. In any event, a similar open α-bromocarbonium ion would be required as an intermediate for the cis olefin isomerization to that required to explain nonstereospecific addition.

iii. β-*tert*-Butylstyrenes.—Even more surprising than the stilbene results are those for the β-*tert*-butylstyrenes. Evidence requiring an open benzylic carbonium ion or, at most, a weakly bridged bromonium ion intermediate in the bromination of the β-methylstyrenes has been discussed previously. A summary of the nonstereospecific adducts in acetic acid is found in Table VII. Our model for the transition state leading to an essentially open ion was the β-*tert*-butylstyrene system. In this case, the 7.6-kcal/mol strain energy in the cis isomer would provide an even larger driving force (than in the β-methylstyrene case) for the rotation apart of the cis substituents, leading to nonstereospecific products.

The stereochemical studies, outlined in Table VII bear out this idea. *trans*-β-*tert*-Butylstyrene gives only 77% anti-addition products relative to 87% for *trans*-β-methylstyrene. An open-ion intermediate is strongly suggested, since even a weakly bridged ion would probably not open and rotate since this would increase any steric interactions. The open ion appears to be attacked predominantly from the side opposite that to which the bromine is first attached, by bromide ion rather than acetic acid, before rotation occurs. A very similar total erythro:threo product ratio is observed for the cis isomer [erythro:threo (cis) = 73:27; erythro:threo (trans) = 77:23]. The predominant syn addition to the cis olefin is strong evidence for the intermediacy of an open ion which tends to rotate to an energetically more favorable conformation before ion-pair collapse or solvent attack occurs. (Neither olefin isomerizes under the reaction conditions, so that the syn-addition products do not arise from isomerization followed by anti addition.) However, the same intermediate and complete equilibration of all ion pairs from both olefins evidently does not occur since nonidentical product distributions are observed. For example, very little solvent incorporation is observed from the trans olefin.

Despite the fact that an open-ion intermediate is clearly involved in the case of the β-*tert*-butylstyrenes, the thermochemical–kinetic results demonstrate that this pair shows very similar trends in both enthalpy and entropy of activation terms to the other olefin pairs. Thus, the $\Delta H^{\neq}$ of the cis isomer is significantly larger than that for the trans, and the enthalpy difference between the isomers increases from 7.6 kcal/mol to 10.8 kcal/mol in going from initial to transition state.

Again, this demonstrates that not only is no rotation allowed at the transition state leading to the open ion, but also that the interacting cis substituents are forced more closely together. The favorable enthalpy of activation with respect to the trans isomer outweighs its more unfavorably negative entropy of activation and the difference in free energy of activation is negative (leading to a $k_c/k_t < 1$). Thus, even in cases where the bromination intermediate is clearly either an open or at best very weakly bridged ion, the transition state nevertheless more closely resembles a cyclic bromonium ion structure (type II or III).

iv. Cyclooctenes.—This cyclic olefinic pair can only be considered through product stereochemical studies since rate studies were not possible. Previous work[27] has shown that the cis isomer reacts normally, probably *via* a cyclic bromonium ion leading to the *trans*-1,2-dibromocyclooctane, essentially exclusively. A small amount of addition–elimination[27b] and transannular rearrangement[27c] has been observed. Such a scheme would be reasonable for this olefin, the more stable of the pair. Also, as previously reported,[27a,c] the trans isomer gives a very complex product mixture. However, in this case also, the mechanism has been proposed to involve a cyclic bromonium ion intermediate, at least initially.[27c] However, the observation, in the present study, of the presence of some trans 1,2 dibromide (by a syn addition) would require olefin isomerization in the presence of bromine or that an open ion must be formed before the product-forming step. Such conclusions remain very tentative.

Overall Reaction Profiles.—Little information can be obtained from the literature on the differences in overall ΔG and ΔH of reaction during the bromination of isomeric olefin pairs because the relative ground-state enthalpies of the diastereomeric dibromide adducts is not generally available. However, some data is available in the case of the 2-butenes and the stilbenes. The gas phase brominations of *cis*- and *trans*-2-butene lead to the diastereomeric *dl*- and *meso*-2,3-dibromobutanes, respectively. It is found that the enthalpy difference of the olefins (-0.95 kcal/mol)[11] is completely removed on formation of the products[28] (within experimental error, the enthalpy difference of the adducts is zero). In the case of the silbenes, the ground-state free-energy difference between the olefins of -3.7 kcal[19] is reduced to only -0.8 kcal on forming the corresponding dibromides.[29] Therefore there is probably only a very small enthalpy difference between the diastereomeric products.[30] It thus seems reasonable that both enthalpy and free-energy differences will generally be small at the product stage of these electrophilic additions.

It is now possible to construct overall reaction profiles on both an enthalpy and free-energy basis, as shown schematically in Figure 1a for the bromination of *cis*- and *trans*-stilbene. These show the following general characteristics. The significant isomeric enthalpy gap which exists at the reactant stage is either retained or shows a definite increase at the transition state in all cases and is then reduced almost to zero at the product stage. (Also the larger the initial enthalpy difference, the more it seems to be increased as the transition state is approached.) On the other hand, the initial *free-energy* difference may decrease smoothly from reactants to products in some cases (*e.g.*, for the

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(27) (a) A. C. Cope, R. A. Pike, and C. F. Spenser, *J. Amer. Chem. Soc.*, **75**, 3213 (1953); (b) G. Wittig and H-l Dorsch, *Justus Liebigs Ann. Chem.*, **711**, 46 (1968); (c) K. Ziegler and H. Wilms, *ibid.*, **569**, 1 (1950).

(28) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Amer. Chem. Soc.*, **60**, 2764 (1938).

(29) W. K. Kwok, I. M. Mathai, and S. I. Miller, *J. Org. Chem.*, **35**, 3420 (1970).

(30) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw Hill, New York, N. Y., 1962; Chapter 6, pp 138–139. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965. Chapter 1, pp 23–26.

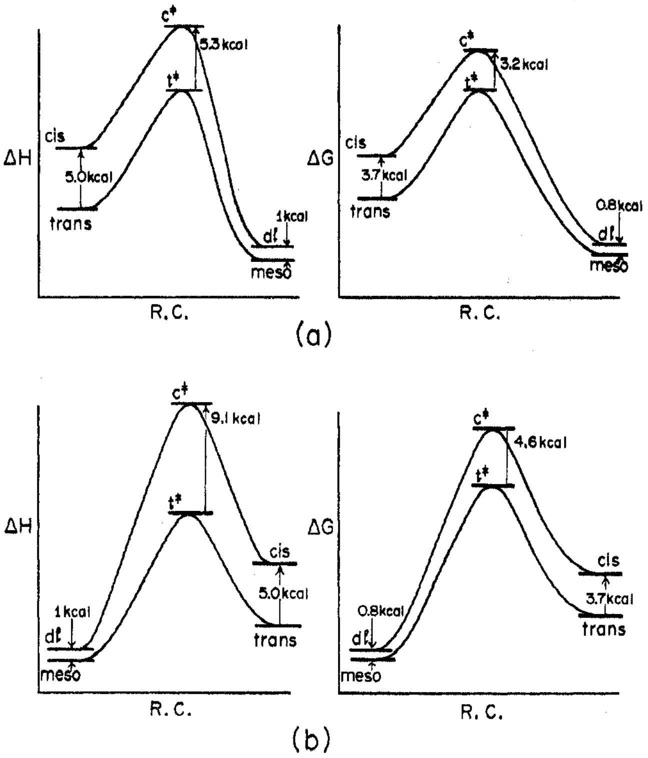

Figure 1.—Schematic representations of enthalpy and free-energy differences along the reaction coordinate for (a) bromine additions to *cis*- and *trans*-stilbene in acetic acid (this work) and (b) LiBr-catalyzed debrominations of *dl*- and *meso*-stilbene dibromides in DMF (ref 29).

stilbenes as shown in Figure 1a) yet in others show a definite increase (*e.g.*, for the *tert*-butylstyrenes or di-*tert*-butylethylenes) at the transition state.

Although halide ion catalyzed debrominations are not exactly the microscopic reverse of the above additions, Miller and coworkers have observed[29,31] analogous results for these reactions. In several cases, they found that the free-energy differences of the reactants (*meso*- and *dl*-stilbene dibromide; $\Delta G = -0.8$ kcal/mol) and the products (*trans*- and *cis*-stilbene, $\Delta G = -3.7$ kcal/mol) did not bracket the difference found at the transition state.[32] That is, transition-state free-energy differences of less than -3.7 kcal/mol were observed. If the enthalpy difference of the dibromides is also fairly small, say, approximately equal to -1 kcal/mol, with the enthalpy difference of the stilbenes known to be -5.0 kcal/mol, then a similar result is found on an enthalpy basis in Miller's work as shown in Figure 1b. For the NaI-[31] and the LiBr-catalyzed[29] debrominations of stilbene dibromides in dimethylformamide, the enthalpy differences at the transition states are -6.8 and -9.1 kcal/mol, respectively. Results from the present study on bromination of this olefin pair show the enthalpy difference to increase by 0.3 kcal/mol and the free-energy difference to decrease by 0.5 kcal/mol from the ground-state olefins to the bromination transition state. These effects may be seen more clearly in Figures 1a and 1b where the enthalpy and free energy are plotted schematically *vs.* the reaction coordinate for the olefin brominations in acetic acid (this work) and for the LiBr-catalyzed debromination of the stilbene dibromides in DMF.[29]

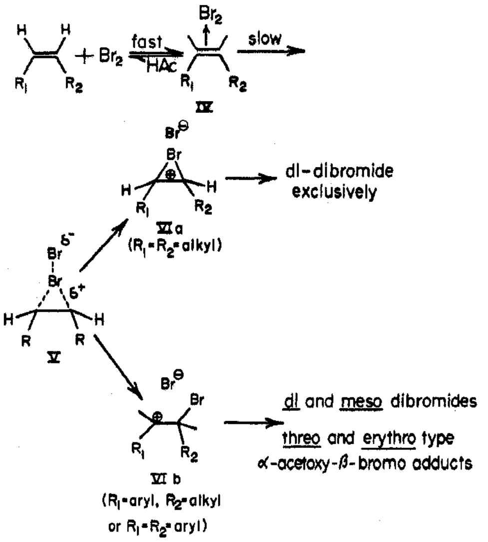

Figure 2.—General mechanistic scheme for bromine additions to cis-1,2-disubstituted olefins.

Thus the findings of this study in which the ground-state enthalpy difference between a pair of isomeric olefins is found to increase initially at the bromination transition state and then to decrease on formation of the products are not without parallel. All the results appear to be consistent with the general mechanistic scheme, shown for a cis olefin in Figure 2. An analogous scheme can be written for the trans isomer. The first step is a rapid preequilibrium formation of a charge-transfer complex (IV). This then proceeds to a highly dipolar transition state (V), which possesses a cyclic bromonium ion like geometry in which the groups R are forced somewhat closer together than in the starting olefin. If the groups R are both either hydrogen or alkyl, continued solvent stabilization allows formation of the bromonium bromide ion-pair intermediate (VIa). Bromine bridging is still retained, in the absence of any more effective mode of stabilization than by the alkyl groups. This ion pair can then collapse directly (without rotation), by bromide attack on the opposite face, to give exclusively the *dl* dibromide.[34]

If one or more of the groups R is a phenyl group, the bromonium ion like transition state (V) proceeds to an essentially open α-bromocarbonium ion intermediate (VIb) in which conjugative stabilization is gained and in which rotation is possible. This ion pair can then collapse to give both *dl* and meso dibromide, whose relative amounts depend on starting olefin structure and solvent. Also solvent attack can occur at the α carbon to give both diastereomeric solvent-incorporated products, which are both completely regiospecifically formed (*i.e.*, exclusively α-acetoxy-β-bromo derivatives).

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[31] I. M. Mathai and S. I. Miller, *J. Org. Chem.*, **35**, 3416 (1970); W. K. Kwok and S. I. Miller, *J. Amer. Chem. Soc.*, **92**, 4599 (1970).

[32] Although Miller has stated that such results are contrary to Hammond's postulate, the very similar results observed in the present study appear to have a reasonable mechanistic interpretation. However, Miller also pointed out that this type of result is analogous to a Brønsted α outside the range of 0–1. If it were generally found that $\Delta\Delta G^{\ddagger}$ need not lie between $\Delta\Delta G$ (reactants) and $\Delta\Delta G$ (products) this would cast further serious doubt[33] on the validity of Brønsted relationships.

[33] F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, **93**, 511 (1971).

[34] In the presence of external added nucleophile, the bromide ion can be replaced in this ion pair, to give mixed products. However, although such counterion exchange presumably involves solvent-separated ion pairs also, solvent does not attack the bromonium ion to give any significant amount of solvent incorporated product.

Experimental Section

All melting and boiling points are uncorrected. Nmr spectra were measured with a Varian A-60 or T-60 spectrometer using samples of roughly 10% solution in CCl_4 containing 1% TMS. A Varian HA-100 instrument was used to measure coupling constants and ^{13}C–H coupling side-band spectra. Liquid samples were purified by repeated distillation through a 24 in. spinning-band column. Analytical glpc was carried out on a Carlo Erba Fractovap Model GI gas chromatograph equipped with a flame ionization detector and disc integrator.

Materials.—The purification of acetic acid has been described previously. Only samples with fp $\geq$16.55° (lit.[35] fp 16.63°) were used as solvent in the kinetic experiments. Commercially available bromine (Anachemia) was used without further purification.

trans-Stilbene (BDH) was recrystallized from ethanol and dried over P_2O_5 at 100° under high vacuum: mp 126.5–126.7° (lit.[36] mp 124.5–124.8°). *cis*-Stilbene was distilled and a colorless center fraction was used for kinetic measurements: bp 106° (17 mm) [lit.[15] bp 145° (10 mm)]. Each isomer was found to be $\geq$99.8% pure by glpc analysis (6 ft × 0.25 in. 20% DGGS on Chromosorb W, 200°, He flow rate 170 ml/min).

cis-Diisopropylethylene (2.5-dimethyl-3-hexene) (Chemical Samples) was distilled: bp 95.0–95.5°, $d^{25}{}_4$ 0.6896 g/ml. The trans isomer (Chemical Samples) was also distilled: bp 98.5° (lit.[37] bp 102°), $d^{25}{}_4$ 0.7065 g/ml (lit.[37] 0.706 g/ml). Glpc analysis [13 ft × 0.25 in. Tide (Procter and Gamble), 71°, 65 ml/min] showed no detectable (<0.5%) impurities in either isomer.

cis-tert-Butylethylethylene (2,2-dimethyl-3-hexene) (Aldrich) was carefully distilled: bp 102.0–102.6° (lit.[37] bp 105.4°), $d^{25}{}_4$ 0.7080 g/ml (lit.[38] 0.7086 g/ml). Glpc analysis under the above conditions showed 0.8% of the trans isomer to be present as the only detectable impurity. This amount has a negligible effect on combustion, solution and kinetic results. The trans isomer (Aldrich) was also distilled: bp 96.5–97.0° (lit.[37] bp 100.9°), $d^{25}{}_4$ 0.6965 g/ml (lit.[37] 0.6995). Glpc analysis showed the only detectable impurity was 0.3% of the cis isomer. Further purification was not attempted.

cis-Di-*tert*-butylethylene (2,2,5,5-tetramethyl-3-hexene) was prepared by the method of Hennion and Banigan.[38] Repeated careful distillation of the final product gave bp 139.0–135.5° (lit.[38] bp 144.2–144.4°); nmr spectrum δ 1.17 (s, 9 H), 5.15 (s, 1 H); ir peaks at 1635 (w), characteristic of nonconjugated C=C stretching, and at 730 cm^{-1} (s), characteristic of *cis*-C=C—H out-of-plane deformation. Glpc analysis (6 ft × 0.25 in. 20% Apiezon L on Chromosorb P, 150°, 100 ml/min) showed the product to be 99.8% pure. *Anal.* Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.62; H, 14.43. *trans*-Di-*tert*-butylethylene was prepared by the method of Puterbaugh and Newman.[39] Purification of the final product by column chromatography (2 ft × 1.8 in. Florisil column, pentane) yielded material with bp 124–126° (lit.[39] bp 125.0°); nmr spectrum δ 0.99 (s, 9 H), 5.32 (s, 1 H); ir negligible absorption in the C=C stretching region, but a strong peak at 980 cm^{-1}, characteristic of a *trans*-HC=CH grouping. Repeated, careful distillation increased the isomer purity to 99% and no further purification was attempted.

cis-Cyclooctene (Matheson Coleman and Bell) was distilled: bp 137° (lit.[38] bp 138°). Glpc analysis (Apiezon L, 110°, 100 ml/min) showed roughly 1% impurity with longer retention time than that of the cis olefin (which is probably not the trans isomer). No further purification was attempted. The trans isomer was synthesized by the method of Cope and coworkers.[27a] Final distillation of the product yielded pure *trans*-cyclooctene: bp 61–62° (43 mm), 142–144° (760 mm) [lit.[36] bp 143° (760 mm)]; nmr δ 0.5–2.9 (m, 12 H), 5.1–5.9 (m, 2 H), no detectable cis peaks; ir strong absorption at 845 and 790 cm^{-1}, characteristic of the trans olefin but only very small peaks at 890 and 755 cm^{-1} due to cis impurity. *Anal.* Calcd for C_8H_{15}: C, 87.19; H, 12.81. Found: C, 87.30; H, 12.76. The trans olefin was purified again immediately before use.

cis-β-tert-Butylstyrene (3,3-dimethyl-1-phenyl-1-butene) was synthesized by the catalytic hydrogenation of the corresponding acetylene, prepared as follows. To a solution of ethyl magnesium bromide (1.0 mole) in 200 ml of ether, cooled to 0°, was added dropwise, a solution of 91.0 g (0.89 mol) of phenylacetylene (Aldrich) in 100 ml of ether. The solution was then allowed to warm to room temperature and was refluxed with stirring, for 14 hr. To this solution, cooled in ice, 113.2 g (0.83 mol) of *tert*-butyl bromide in 100 ml of ether was added dropwise (4 hr). After warming to room temperature, the solution was refluxed for 20 hr and allowed to cool. Work-up was achieved by cautiously pouring this solution into 500 ml of ice and 1 *N* HCl and was followed by extraction with ether. Concentration of the dried ether extracts, followed by vacuum distillation, gave two fractions. The first fraction, boiling range of 43–53° (17 mm), consisted of unreacted phenylacetylene, 31.6 g (0.31 mol). The second fraction, boiling range of 83–97° (17 mm), consisted mostly of the desired *tert*-butylphenylacetylene: 64.6 g (0.41 mol, 45% yield); nmr δ 1.31 (s, 9 H), 7.0–7.5 (m, 5 H). This crude material was used directly in the hydrogenation. Optimum conditions involved shaking a mixture of 50.1 g of *tert*-butylphenylacetylene (0.25 mol), 1 g of freshly prepared Raney nickel catalyst, and 150 ml of 95% ethanol with an average H_2 pressure of 55 psi until 1.1 equiv of H_2 had been consumed (6 hr). This yielded 36 g of crude material which was analyzed by nmr and glpc, which revealed the presence of roughly 65% *cis-β-tert*-butylstyrene, 10% unreacted acetylene, 20% 3,3-dimethyl-1-phenylbutane, and 5% *trans-β-tert*-butylstyrene. The four compounds were cleanly separable by glpc (Carlo Erba, DEGS column at 125°, He flow rate 130 ml/min). The product was purified by two careful spinning-band distillations with the cis olefin being concentrated in the initial fractions. The final distillation yielded 12 g of the pure *cis-β-tert*-butylstyrene: bp 81–82° (14 mm) [lit.[40] bp 80.5–81.0° (16 mm)]. Glpc analysis on the DEGS column at 110° showed that no detectable impurities were present (>99.9% pure). A strong ir absorption at 698 cm^{-1}, characteristic of the C—H out-of-plane deformation frequency of the *cis*-HC=C—H grouping, was present. The nmr spectrum [δ 0.98 (s, 9 H), 5.55 (d, J = 12.8 Hz, 1 H), 6.40 (d, J = 12.8 Hz, 1 H); 7.17 (s, 5 H)] is consistent with the cis structure. The olefin hydrogens appear as an AB quartet; the cis-olefinic coupling of 12.8 Hz is in the range expected. *Anal.* Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.92; H, 9.91. *trans-β-tert*-Butylstyrene was prepared by the acid-catalyzed isomerization of the cis isomer. About 15 g of a hydrocarbon mixture from the cis-olefin preparation, enriched in the cis isomer, was refluxed in 20 ml of acetic acid with a catalytic amount of *p*-toluenesulfonic acid. After 18 hr, the solution was cooled and poured into a mixture of 50 ml of pentane and 50 ml of water. Work-up was achieved in the usual way. Concentration of the dried pentane solution yielded *trans-β-tert*-butylstyrene: bp 91–92° (11 mm) [lit.[40] bp 90–91° (13 mm)]. Glpc analysis on the DEGS column at 110° showed no detectable impurities were present (>99.9% pure). A strong ir absorption at 967 cm^{-1}, characteristic of the C—H out-of-plane deformation frequency in the *trans*-H—C=C—H arrangement, was present. The nmr spectrum showed δ 1.13 (s, 9 H), 6.22 (s, 2 H), 7.0–7.5 (m, 5 H). The olefinic hydrogens appear to be almost coincident. At higher amplitude however, two weak peaks 16.5 Hz to either side of the δ 6.22 are detectable. Thus, these two hydrogens are not identical; the very tightly coupled AB spectrum indicates roughly a 16.5-Hz coupling, indicative of the trans structure. Similarly, the fact that the *tert*-butyl in the trans olefin occurs at lower field than that in the cis olefin (δ 1.13 *vs.* 0.98, respectively) supports the assigned geometry. *Anal.* Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.89; H, 10.04.

The *cis*- and *trans*-2-butenes were commercially available and used without further purification (in previous studies[2] they were found to be <99.5% pure). The 3-hexenes and 1-hexene (Chemical Samples) were spinning band distilled before use.

Heats of Combustion.—All heats of combustion were mea-

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[35] "Techniques of Organic Chemistry," Vol. III, 2nd ed, p 145. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Ed., Interscience, New York, N. Y., 1955.

[36] "Handbook of Chemistry and Physics," 51st ed, R. C. Weast, Ed, Chemical Rubber Co., Cleveland, Ohio, 1970.

[37] R. R. Dreisbach, "Physical Properties of Organic Compounds," *Advan. Chem. Ser.*: Vol. I (1955), Vol. II (1959), Vol. III (1961). "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," NBS Circular C461, API Project 44, Washington, D. C., 1947.

[38] G. F. Hennion and T. F. Banigan, *J. Amer. Chem. Soc.*, **68**, 1202 (1946).

[39] W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **81**, 1611 (1959).

[40] K. Yasufuku, S. Hirose, S. Nozakura, and S. Murahadu, *Bull. Chem. Soc. Jap.*, **40**, 2139 (1967).

sured with a Parr 1231 oxygen bomb calorimeter equipped with a Model 2601 adiabatic control unit. A Parr 1111 oxygen bomb was used to contain samples, and temperatures were measured with Parr 1622 calibrated 24–30° thermometers. Solid samples were pelletized and ignited in open stainless steel crucibles. Liquid samples were sealed in a volatile sample holder (Parr A 158A) immediately after weighing to prevent evaporation losses. Samples were weighed and stored in the presence of P_2O_5 to prevent absorption of atmospheric water. Combustions were normally performed using 30-atm O_2 pressure, except for the β-*tert*-butylstyrenes where 35 atm was found necessary to prevent considerable soot formation, indicating incomplete combustion. Corrections for small amounts of soot formation were made in all cases. Corrections were made for combustion of residual N_2 in the bomb by titrating for nitrous and nitric acids.[41] The calorimeter was carefully calibrated using Parr-certified benzoic acid pellets, which yielded under standard bomb conditions (30-atm O_2; reference $T = 25°$; bomb volume 0.360 l.) a heat of combustion value of -6323.6 cal g^{-1}.[41] All calibration runs were corrected to standard bomb conditions using the "Washburn" correction terms, as recently revised and expanded.[42] Full experimental details and typical experimental data and calculations are available in the Ph.D. thesis of R. S. M. (University of Toronto).

Heats of Solution.—Heats of solution were measured by rapidly dissolving weighed amounts of the olefins in a fixed quantity of anhydrous acetic acid, using a simple calorimeter. (The calorimeter was calibrated using pyridine whose heat of solution at infinite dilution at 25° is known. The reported value[43] of 6.50 kcal mol^{-1} was assumed to be accurate to within 5%.) This consisted of a 250-ml dewar flask, tightly covered with a two-hole stopper. One hole was fitted with a Parr certified 24–30° thermometer and the other was used for syringe injection of the olefin samples. Solvent was added to the calorimeter and thermal equilibration at or near 25° was allowed, with continuous (magnetic) stirring. After the equilibration period "initial" temperature readings were taken every 1–2 min to the nearest 0.001°. These usually drifted very slightly but linearly, with time, typical drifts being of the order of ±0.003–0.006°/min. The last "initial" temperature was noted and the olefin sample (1–2 g) was then injected rapidly, solution being complete within a few seconds as noted by the rapid temperature changes. The first "final" temperature reading was taken after 1 min and time–temperature readings were continued for 20–25 min. The initial and final calorimeter temperatures were then obtained by extrapolation to the mixing time, by use of the linear time–temperature plots before and after solution of the olefin. For each experiment a temperature correction was made because the olefin and solvent were at different initial temperatures. This was based on the known specific heats of the acid and olefins.[37,44]

Multiple injections of sample into the same solution, use of different sample sizes, and different initial temperatures showed no trends in the calculated heats of solution. This confirms that the measured heats of solution are effectively those at infinite dilution. These were reproducible to within 0.1 kcal mol^{-1}, except for *trans*-stilbene. This was the only solid olefin used, and the results were more difficult to obtain accurately. In this case reproducibility to within only 0.3 kcal mol^{-1} could be obtained.

Kinetic Measurements.—The experimental details involved in the stopped-flow kinetic measurements of the bromination of the more reactive olefins have been previously described.[45] Pseudo-first-order rate plots (*i.e.*, with 50–200-fold excess olefin) were linear over at least 75% reaction, with correlation coefficients of 0.999 or better. Initial bromine concentrations were kept in the range $2.5\text{–}5.0 \times 10^{-4}$ *M* to minimize any contribution from the parallel third-order process (see accompanying paper). Unfortunately *trans*-cyclooctene reacted too rapidly to give reliable rate plots and probably has $k_2 \geq 5 \times 10^6$ l. m^{-1} sec^{-1}. The rates of bromination of the less reactive olefins (*i.e.*, stilbenes) were measured conventionally using a Cary 16 spectrophotometer, by following the disappearance of Br_2 absorption at 490 nm, again under pseudo-first-order conditions.

Product Analysis.—The main purpose of the product studies on the olefinic pairs was to determine the degree of stereospecificity of the dibromides and acetoxybromides formed in the bromination process. Nonstereospecific addition was accompanied by checks on starting isomer stability under the reaction conditions. Analyses were routinely carried out by combined glpc–nmr techniques and extensive purification and physical property measurements were usually not attempted. Yields quoted are those from nmr or glpc analyses.

Product runs in acetic acid under conditions where the second-order process is dominant were carried out as follows. One gram of the olefin in a rapidly stirred solution in 20 ml of acetic acid was protected from the light while 1 equiv of bromine in 20 ml of acetic acid was added dropwise. The bromine concentration was kept as low as possible during addition so that the k_2 term would dominate.[45] This was easily controlled with the reactive olefins and addition was normally complete after 2–3 hr. Work-up was achieved by pouring the solution into a 50% mixture of water and pentane. Any excess bromine was destroyed by the addition of a few crystals of $Na_2S_2O_3$. The pentane layer was removed and washed successively with water, saturated aqueous $NaHCO_3$ until neutral, and finally with water. Drying over $MgSO_4$ and then evaporation yielded the crude product. The rather insoluble stilbene dibromides were isolated by pouring the acetic acid solution into water and filtering off the precipitate. The solid was washed with water and acetic acid and finally air dried. Analyses were performed by nmr on the reaction mixtures themselves.

Diisopropylethylenes.—The major product of the bromination of the trans isomer in acetic acid is the meso dibromide: 83% yield by glpc analysis (5-ft DEGS column at 105°, He 65 ml/min). Preparative glpc (13-ft TIDE column at 80°, He 65 ml/min) yielded a white crystalline solid: mp 53–54° (for the meso dibromide, lit.[46] mp 54–55°). *Anal.* (of the purified dibromide): Calcd for $C_8H_{16}Br_2$: C, 35.32; H, 5.93; Br, 58.75. Found: C, 35.76; H, 5.85; Br, 56.89. Some of the dibromides became slightly yellowish shortly after purification, owing to loss of bromine. Thus, some of the bromine analyses were too low. The nmr spectrum showed δ 0.91 (d, $J = 6.5$ Hz, 6 H), 1.08 (d, $J = 6.5$ Hz, 6 H), 2.53 (m, 2 H), 4.16 (t, $J = 1.0$ Hz, 2 H). The isopropylmethine hydrogen appears as a septet with further splitting by the bromomethine hydrogen. The isopropyl methyls, adjacent to the asymmetric center, are nonequivalent. The theoretical 12-line AA'XX' spectrum[47] appears as an A_2X_2 where the equivalent bromomethine hydrogens show an apparent average coupling of 1.0 Hz with the isopropylmethine hydrogens. Decoupling the multiplet centered at δ 2.53 sharpens the 4.16 to a singlet, while decoupling the 4.16 triplet gives a sharp septet at 2.53. The magnitude of the vicinal coupling constant between the bromomethine hydrogens has frequently been used[2,44,46,48] as a criterion for distinguishing meso–*dl* and erythro–threo diastereomeric pairs. An examination of the steric and electrostatic interactions reveals that in the preferred rotamer of the meso dibromide, the vicinal hydrogens bear an anti relationship to one another. Anti-hydrogen couplings for compounds of this type are normally in the range 10–11 Hz while gauche couplings are usually 2–4 Hz. Thus, a large vicinal coupling constant would be expected for the meso dibromide. (No clear-cut distinction is possible on the basis of relative rotamer populations for the *dl* dibromide.) The nmr spectrum of a very concentrated solution of the purified meso dibromide in the ^{13}C–H splitting side-band regions ($J_{^{13}C\text{–}H} = 153$ Hz) of the bromomethine hydrogens gave a doublet of doublets ($J = 11.8$ and 1.9 Hz) for the H–^{13}C(Br)–^{12}C(Br)–H grouping. The larger coupling is assigned to the vicinal $J_{AA'}$ coupling while the smaller must be the J_{AX} splitting. If $J_{AX'}$ is zero, then the observed average $J_{AX(X')}$ for the A_2X_2 system would be $(1.9 + 0)2 \simeq 1.0$ Hz, as observed. An nmr spectrum of the crude product from the trans olefin revealed the presence of 20% meso dibromide and 80% acetoxybromide. This latter compound was purified by preparative glpc on the Tide column to yield a colorless oil. The ir spectrum showed the intense sharp carbonyl

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[41] J. Coops, R. S. Jessup, and K. van Nes, "Experimental Thermochemistry," Vol. I, F. D. Rossini, Ed., Interscience, New York, N. Y., 1956, Chapter 3.

[42] E. W. Washburn, *Nat. Bur. Stand. J. Res.*, **10**, 525 (1933), and ref 41, Chapter 5.

[43] Reference 17, p 152.

[44] Reference 17, pp 101–113.

[45] K. Yates, R. S. McDonald, and S. A. Shapiro, *J. Org. Chem.*, **38**, 2460 (1973); see accompanying paper.

[46] J. R. Chretien, Doctoral Thesis, University of Orleans, France, 1971.

[47] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Elmsford, N. Y., p 392.

[48] C. A. Kingsbury and D. C. Best, *J. Org. Chem.*, **32**, 6 (1967).

absorption at 1750 cm^{-1}; nmr spectrum δ 0.8–1.1 (m, 12 H), 2.03 (s, 3 H), 2.1–2.7 (m, 2 H), 3.91 (d of d, J = 2.0, 10.2 Hz, 1 H), 5.08 (d of d, J = 2.8, 10.2 Hz). The methyl peaks near δ 1 are an overlapping series of four doublets, since all are nonequivalent. The bromomethine hydrogen causes the δ 4 resonance, and the acetoxymethine the δ 5 peak. The vicinal dimethine coupling is 10.2 Hz, and, by similar arguments on the basis of rotamer populations to those above, this acetoxybromide can be assigned the erythro stereochemistry.

The acetoxybromides from *trans-* and *cis*-diisopropylethylene were prepared following the method of Jovtscheff.[49] Bromination of the cis olefin in acetic acid gave a white crystalline solid which appeared to be a single compound (>99% pure) by glpc analysis. A sublimed sample had mp 73–74° (for the *dl* dibromide, lit.[46] mp 73°). *Anal.* Calcd for $C_8H_{16}Br_2$: as above. Found: C, 35.46; H, 5.96; Br, 58.17. No carbonyl absorption was observed in the ir spectrum of the crude product in a Nujol mull. Analysis by glpc revealed the absence of the meso dibromide and the erythro and threo acetoxybromides. The nmr spectrum of purified sample showed δ 1.02 (d, J = 6.5 Hz, 6 H), 1.15 (d, J = 6.5 Hz, 6 H), 2.0–2.4 (m, 2 H), 3.70–3.85 (m, 2 H). On the basis of steric and electrostatic effects, no one conformation is clearly predominant for the *dl* dibromide and the $J_{AA'}$ coupling should be smaller than that observed for the meso dibromide. An nmr spectrum of the pure dibromide from the cis olefin in the ^{13}C–H side-band regions ($J_{^{13}C-H}$ = 146 Hz) of the bromomethine multiplet centered at δ 3.77 showed the H–^{13}C–^{12}C–H grouping to give a doublet of doublets (J = 3.5 and 8.2 Hz). The 3.5-Hz coupling was assigned to the isopropyl methine–bromomethine splitting. Thus, the vicinal bromomethine coupling is at most 8.2 Hz, lower than that obtained in the meso dibromide. This dibromide is assigned the *dl* stereochemistry.

The acetoxybromide from the cis olefin, prepared by the method outlined above, was free from any major impurities by glpc analysis. Short-path distillation yielded a colorless liquid: bp 46–47° (0.1 mm). *Anal.* Calcd for $C_{10}H_{19}BrO_2$: C, 47.82; H, 7.62; Br, 31.82; O, 12.74. Found: C, 47.84; H, 7.32; Br, 32.83; O (by difference), 12.40. The nmr spectrum showed δ 0.8012 (m, 12 H), 1.65–2.25 (m, 2 H), 1.99 (s, 3 H), 3.91 (d of d, J = 5.0, 5.9 Hz, 1 H), 4.87 (d of d, J = 5.0, 6.7 Hz, 1 H). An intense carbonyl peak was observed at 1745 cm^{-1} in the ir spectrum. The 5.0-Hz coupling is assigned to the vicinal bromomethine–acetoxymethine splitting. This is lower than the analogous 10.2-Hz coupling found in the erythro isomer; so this compound is assigned the threo-acetoxybromide stereochemistry. None of this compound was detected in either the trans- or cis-olefin product from addition of bromine in acetic acid. The four compounds were separable by glpc (6-m DEGS column at 93°, He 120 ml/min).

***tert*-Butylethylethylenes.**—Bromination of the trans olefin in acetic acid gave one major component in <99% yield by glpc analysis (DEGS column at 90°, He flow rate 100 ml/min). Some addition–elimination products were detected but in trace amounts (<1%). Short-path distillation of the crude reaction mixture yielded a colorless liquid: bp 47–48° (0.13 mm). *Anal.* for a dibromide. Calcd for $C_8H_{16}Br_2$: C, 35.2; H, 5.93; Br, 58.75. Found: C, 35.59; H, 5.94; Br. 58.49. The nmr spectrum showed δ 1.97 (t, J = 7 Hz, 3 H), 1.15 (s, 9 H), 1.7–2.2 (m, 2 H), 4.23 (d of t, J = 6.2, 1.9 Hz, 1 H), 4.38 (d, J = 1.9 Hz, 1 H). The vicinal coupling constant, observed directly from the *tert*-butyl bromomethine hydrogen resonance, is 1.9 Hz, low even for a pure gauche coupling. Very low vicinal coupling constants have been previously observed for the erythro dibromide and dichloride adducts of *tert*-butylmethylethylene (*i.e.*, 2.4 and 2.0 Hz, respectively[48]). Comparing our results with those of these workers, on the basis of both the erythro and threo adducts, this compound is assigned the erythro-dibromide structure. By combined nmr and glpc analysis, under the above conditions, it was found that <1% threo dibromide or either of the acetoxybromides, all independently synthesized, could be present in the bromination product. The acetoxybromide of the trans olefin was prepared by the method outlined above[49] and subjected to short-path distillation: bp 46–47° (0.12 mm). Glpc analysis showed the presence of roughly 5% erythro dibromide in this acetoxybromide, but also that this compound was not present in the trans-olefin product run. No further purification was attempted. The ir spectrum showed an intense carbonyl absorption at 1735 cm^{-1}. The nmr spectrum confirmed the acetoxybromide structure: δ 1.03 (t, J = 7.4 Hz, 3 H), 1.13 (s, 9 H), 1.5–2.0 (m, 2 H), 2.03 (s, 3 H), 3.99 (d, J = 3.1 Hz, 1 H), 4.7–5.1 (m, 1 H). The bromomethine hydrogen on an alkyl substituted carbon is found to resonate in the range of 3.7 4.5[46] while the acetoxymethine hydrogen occurs at 2.7–5.1. In this acetoxybromide the bromomethine hydrogen appears as a doublet (and thus must be on the carbon with the *tert*-butyl substituent) from which the vicinal coupling constant, 3.1 Hz, may be obtained directly. Again, this low coupling constant, characteristic of a gauche hydrogen arrangement, is larger than that in the acetoxybromide obtained from the cis olefin and is assigned the "erythro"[50] stereochemistry. Thus, regiospecific and stereospecific acetoxybromide formation has occurred from the trans olefin. Only one acetoxybromide is observed by glpc or nmr.

Glpc analysis of the crude product from the bromination of the cis olefin showed the presence of two components in the ratio of 92:8. Retention times and nmr spectra of these components were different from those of either of the two compounds characterized above. In fact, <1% erythro dibromide or "erythro" acetoxybromide could be present from glpc and nmr analyses. Short-path distillation yielded a colorless liquid, bp 45–46° (0.08 mm), with no separation of these two components. The nmr of the major component is strongly suggestive of a dibromide: δ 0.8–1.2 (m, 3 H) 1.18 (s, 9 H), 1.6–2.3 (m, 2 H), 3.93 (d, J = 1.6 Hz, 1 H), 3.9–4.3 (m, 1 H). The vicinal coupling constant, 1.6 Hz, is smaller than that observed in the erythro dibromide; so this compound is assigned the threo-dibromide stereochemistry. The structure of the minor component of the reaction mixture was proved by independent synthesis. Treatment of the cis olefin with NBS in acetic acid, followed by work-up and distillation, yielded a colorless liquid: bp 44.0–44.5° (0.12 mm). The ir spectrum revealed an intense carbonyl absorption at 1735 cm^{-1}. Glpc analysis showed the presence of only one component (>99%). Analysis confirmed the compound was the acetoxybromide. *Anal.* Calcd for $C_{10}H_{19}O_2Br$: C, 47.82; H, 7.62; Br, 31.82; O, 12.74. Found: C, 47.80; H, 7.63; Br, 32.08; O (by difference), 12.49. The nmr spectrum [δ 0.6–1.2 (m, 3 H), 1.08 (s, 9 H), 1.3–1.8 (m, 2 H), 2.02 (s, 3 H), 3.89 (d, J = 1.1 Hz, 1 H), 5.00 (d of t, J = 6.9, 1.1 Hz, 1 H)] supports the acetoxybromide structure, where the *tert*-butyl and bromine are attached to the same carbon. The vicinal coupling constant, 1.1 Hz, is lower than that obtained from the "erythro" acetoxybromide; so this compound is assigned the "threo"-acetoxybromide structure. This compound was identified, by comparison of glpc retention times and nmr spectra, as the 8% component in the product run on the cis olefin. These four compounds were all separable by glpc (DEGS column at 90°, He 100 ml/min).

Di-*tert*-butylethylenes.—Work-up of the bromination product of the cis olefin yielded a white crystalline solid which, by glpc analysis (DEGS column at 100°, He 120 ml/min), was >99% a single component. A sample, purified by sublimation, had mp 57–58° and analyzed for a dibromide. *Anal.* Calcd for $C_{10}H_{20}Br_2$: C, 40.02; H, 6.72; Br, 53.26. Found: C, 40.01; H, 6.65; Br, 52.94. The nmr spectrum showed only two hydrogen absorptions: δ 1.13 (s, 9 H), 4.19 (s, 1 H). The high amplitude spectrum in the ^{13}C–H splitting side-band regions of the bromomethine hydrogens ($J_{^{13}C-H}$ = 145 Hz) revealed a doublet (J = 1.0 Hz) for the H–^{13}C(Br)–^{12}C(Br)–H grouping. From this very low vicinal coupling constant, close to that observed for the analogous dichloride assigned the *dl* stereochemistry[24] (0.8 Hz), the *dl*-dibromide structure was assigned to this compound. Treatment of the cis olefin with NBS in acetic acid and nmr analysis of the crude reaction work-up revealed that the major product, an acetoxybromide, was not present in >0.5% yield in the above product run: nmr spectrum of the acetoxybromide δ 0.98 (s, 9 H), 1.05 (s, 9 H), 2.05 (s, 3 H), 3.97 (d, J = 1.0 Hz, 1 H), 4.95 (d, J = 1.0 Hz, 1 H). The very low vicinal coupling constant, 1.0 Hz, again prompted the assignment of the threo stereochemistry. The addition of 1 equiv of bromine to a stirred, light-protected solution of the trans olefin in acetic acid gave a very complex product mixture. Glpc analysis of the crude product showed, other than unreacted trans olefin,

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[49] A. Jovtscheff and S. L. Spassov, *Monatsh. Chem.*, **98**, 2272 (1967).

[50] Although the terms erythro and threo are not strictly applicable to these unsymmetrical ($R_1 \neq R_2$) acetoxybromides, the terms "erythro" and "threo" will be used here so that the stereochemistry of the acetoxybromides can be related directly to that of the analogous dibromides.

four major components with retention times of 1.8, 9.4, 12.4, and 16.5 min. Neither the *dl* dibromide nor the threo acetoxybromide, obtained above from the cis olefin, could be detected by glpc or nmr analysis. The nmr spectrum was similarily uninformative; other than peaks corresponding to the trans olefin ($\simeq$40% after addition of 1 equiv of bromine) there were complex absorptons in the regions of δ 0.9–1.4, 1.6–2.1, and 3.8–4.2. Little, if any, solvent incorporation appeared to have occurred. Complete bromination of the product mixture resulted in the disappearance of the starting material peak and that at 1.8 min in the glpc analysis. This fact, combined with the very short retention time, suggested that this component was a bromo olefin. Treatment of the trans olefin with NBS in acetic acid gave as the major product (>90%), a compound having a retention time of 1.8 min. Purification by preparative glpc (20% SE-30 on Chromsorb P at 200°, He flow rate 70 ml/min) yielded a colorless liquid which, from the elemental analysis and nmr spectrum, was concluded to be the rearranged bromo olefin, 4-bromo-2,3,5,5-tetramethyl-1 hexene. A rearranged chloro olefin of exactly analogous structure has been observed from the chlorination of the trans olefin in CCl_4.[24] *Anal.* Calcd for $C_{10}H_{19}Br$: C, 54.80; H, 8.74; Br, 36.46. Found: C, 55.08; H, 8.75; Br, 36.50. Comparison of the glpc retention time and nmr spectrum of this compound with that of the crude trans-olefin bromination product revealed that this compound was present in the product in roughly 15% yield. No acetoxybromide was observed from the trans-olefin reaction with NBS in acetic acid. An attempt was made to collect pure samples of the longer retention time components from the reaction mixture but the severe glpc conditions required (column temperature <220°) caused considerable decomposition.

Stilbenes.—The crude solid product from the bromination of the trans isomer in acetic acid was highly insoluble in most organic solvents in which an nmr spectrum could be obtained. The solid had a high, sharp melting point, 239–240°, close to that for an independently synthesized sample of the meso dibromide: mp 242–243° (prepared in CH_2Cl_2) (lit.[8] mp 237–239°). The ir spectrum of the crude sample (KBr pellet) gave absorptions at 601 and 551 cm^{-1}, characteristic of the meso dibromide. Those chracteristic of the *dl* dibromide, also synthesized independently [mp 114–115° (lit.[8] mp 110–111°)], at 668 and 574 cm^{-1} were absent. A high amplitude nmr spectrum of a saturated solution of the crude product in CCl_4 showed a very weak resonance near δ 2 characteristic of an acetate. Thus, the trans olefin brominates to form predominantly the meso dibromide with a trace of acetoxybromide, unaccompanied by *dl* dibromide. This is in accord with previous studies by other workers.[8]

The crude product from the bromination of the cis olefin under identical conditions gave a solid which showed softening near 111–112°, the bull of the material melting above 235°. The ir spectrum showed strong absorption characteristic of the meso dibromide, and small *dl*-dibromide peaks. A saturated solution of the crude adduct in CCl_4 gave nmr peaks at δ 1.78 and 2.03 which could be characteristic of the two diastereomeric acetoxybromides. Although no quantitative information can be obtained from this data, it does appear that nonstereospecific but stereoselective syn addition has occurred.[8] A check for olefin isomerization during this run was very informative. An 0.23 *M* solution of *cis*-stilbene in acetic acid was stirred for 2–3 hr at room temperature. There was no detectable isomerization by glpc (DEGS column at 200°, He 170 ml/min). After addition of 1% of the equivalent amount of bromine and stirring until complete reaction, it was found that 6–7% of the olefin was *trans*-stilbene. These conditions would closely resemble those in a kinetic run. No further change in olefin ratio occurred after 3 hr. After addition of 5% of the bromine, roughly 25% isomerization had occurred after 0.5 hr and no further change up to 17 hr took place. After addition of 50% of the equivalent amount of bromine, 90% of the unreacted olefin was the trans isomer after 0.5 hr, while, after 24 hr and complete reaction, all unreacted olefin was the *trans*-stilbene. Thus, it is likely that the lack of stereospecific addition to the cis olefin is at least partly due to isomerization under the bromination conditions.

β-tert-**Butylstyrenes.**—Both isomers were stable in acetic acid for 24 hr. Less than 1% of the other isomer could be detected by glpc or nmr analysis. The dibromides and acetoxybromides were too involatile for glpc analysis; thus all analyses were carried out by nmr. The dibromides were prepared by the slow addition of a bromine to the stirred, light-protected olefin solution in CCl_4. Oxygen was continuously bubbled through the solution during the reaction. Work-up simply involved removal of the solvent by evaporation. The acetoxybromides were prepared by the NBS–acetic acid method[49] previously described. All adducts were of the 3,3-dimethyl-1 phenyl 1,2 dibromo (or 1 acetoxy 2 bromo) butane type. Both the erythro and threo diastereomers of both compounds were observed and characterized by their nmr spectra. No peaks other than those attributed to these four compounds or unreacted starting material were observed. Product ratios were measured by repeated integrations of the appropriate nmr resonances.

Two dibromides were produced in a 4:1 ratio from the bromination of the trans-olefin in CCl_4. The fact that major dibromide has the larger vicinal coupling constant, 4.6 Hz, relative to 2.0 Hz for the minor component, led to the assignment of the erythro stereochemistry to this major product. The minor component is assigned the threo-dibromide structure. The same two dibromides are formed in a 2:1 ratio from the bromination of the cis isomer in CCl_4. Again the erythro dibromide is the major product, but now a higher proportion of the threo adduct formed supports the stereochemical assignments.

The NBS method on the trans olefin produced two acetoxybromides in the ratio of 11.5:1. The nmr data again suggest the predominant product is the "erythro" acetoxybromide since it has the large vicinal coupling constant, 6.7 Hz, relative to 1.9 Hz for the minor component, assigned the "threo" acetoxybromide structure. These diastereomers are produced in a 1:6.7 ratio from the cis olefin; again the higher proportion of the "threo" adduct supports the assigned structures.

The bromination of these olefins in acetic acid (under predominant k_2 conditions[46]) gave all of the above adducts. The trans isomer produced a 3.3:1 ratio of the erythro and threo dibromides, respectively (98% of the product), along with 2% "erythro" acetoxybromide. The cis isomer produced a 2.2:1 ratio of these dibromides (80% of the product) and a 9:1 ratio of the "erythro" and "threo" acetoxybromides, respectively.

Aliquots of one of the bromination runs of the cis olefin in acetic acid were checked by nmr to test for isomerization. No detectable (>5%) isomerization of the cis to trans olefin had occurred up to 60% reaction. Thus, the lack of stereospecificity is *not* due to isomerization of the starting material.

Cyclooctenes.—Bromination of the cis isomer in acetic acid gave one major product (>90%) by glpc (DEGS column at 135°, He 130 ml/min). Short path distillation of the crude product afforded a colorless liquid, bp 63–66° (0.02 mm) [for *trans*-1,2-dibromocyclooctane, lit.[27a] bp 89–91° (at 0.5 mm)], which turned yellow on standing. The dibromide appears to liberate bromine spontaneously. The nmr of the freshly distilled compound was taken: δ 1.2–2.8 (m, 12 H), 4.3–4.8 (m, 2 H). The crude product also showed a small acetate signal at δ 1.93 which may be present in 2–3% yield. No elimination products were detectable.

Bromination of the trans olefin in acetic acid proceeded with HBr evolution indicative of considerable solvent incorporation or addition–elimination. The crude work-up revealed, by glpc analysis, the presence of at least nine components other than unreacted olefin. The complex nmr spectrum revealed only very small peaks near δ 2 indicative of very little solvent incorporation. Three peaks of retention time $\leq$2.5 min reveal the presence of significant amounts of elimination products (bromo olefins, $\simeq$35% yield). One such product could be 3-bromocyclooctene,[27b] but transannular reactions also have been reported during the bromination of medium-ring olefins.[27c] Thus, other olefins formed by a 1,4 hydride transfer followed by elimination could be present. Three peaks of retention times expected for the dibromides (8.3, 9.8, and 11.3 min) were also detected. The latter has the same retention time as the trans dibromide obtained from the cis isomer. None of the cis-1,2 dibromide has been previously detected but two rearranged dibromides, 1,3-dibromo-2-methyl- and 1,4-dibromo-5-methylcycloheptane, have been detected.[51] These dibromides account for 60% of the product mixture; the remaining 5% is probably an acetoxybromide or a secondary reaction product of the bromo olefins. Such a complex reaction mixture from the trans olefin, together with Hbr formation, has been previously reported.[27c,51] Not all of the products have been characterized and extensively studied here since the kinetic work on this olefin could not be carried out.

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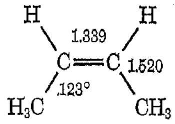
(51) N. L. Allinger and L. A. Tushams, *Tetrahedron*, **23**, 2051 (1967).

Registry No.—4-Bromo-2,3,5,5-tetramethyl-1-hexene, 40087-55-6; *trans*-β-methylstyrene, 873-66-5; *cis*-β-methylstyrene, 766-90-5; 1-hexene, 592-41-6.

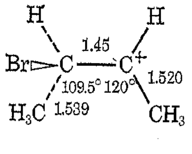
Appendix

Geometrical Calculations.—The reasonable assumption is made that all of the ground-state enthalpy difference between cis- and trans-1,2-disubstituted ethylenes is due to the unfavorable steric interaction between substituent groups in the cis isomer. The trans isomer and its possible reaction intermediates should be essentially free of such steric effects. Thus formation of intermediates (or transition states) from the cis olefin, in which the distance between the 1,2 substituents has decreased, should result in an increase in the isomeric enthalpy difference established in the initial states, while, for those in which this distance is increased, there should be a decrease (or even disappearance) of the isomeric enthlapy difference.

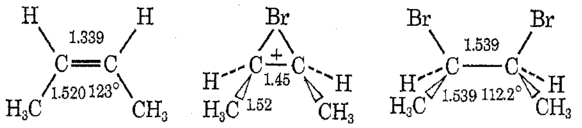
In an attempt to test the premise that type I intermediate geometry (*i.e.*, open α-bromocarbonium ion) would decrease the steric effects from those present in the olefins, whereas type III geometry (cyclic bromonium ion) would increase them, calculations of interatomic distances were carried out using the 2-butene system as a model. Geometries of molecules were taken from the literature;[52] those for ionic species were estimated using standard trigonal or tetrahedral bond angles and bond lengths optimized from *ab initio* calculations.[53] Based on the geometry shown for *cis*-2-butene, the methyl(carbon)–methyl(carbon) distance is 2.995 Å, whereas, in the trans isomer, this distance is 3.933 Å.



The geometry of an initially formed (*i.e.*, before rotation) α-bromocarbonium ion was taken to be as shown, where the methyl group on the tetrahedral carbon is 30° below the plane of the other three carbons. The methyl–methyl distance[54] in this ion is 3.057 Å, which increases to 3.154 and 3.255 Å, with small rotations of 10 and 20°, respectively, about the central C–C bond, in the direction which relieves steric effects. Thus, even if no rotation were allowed at the transition state leading to the open ion, it seems clear that the steric interaction between adjacent groups would be expected to decrease from that in the starting olefin. Even assuming central bond length of 1.41 Å for this ion, which is very short for a $C(sp^2)$–$C(sp^3)$ bond, the distance between the *cis*-methyl groups is still significantly greater (3.017 Å) than in the olefin.



Calculation of the corresponding methyl–methyl distance in the cyclic bromonium ions (of type III) is more difficult. The problem is to estimate a reasonable geometry for this ion. The central carbon–carbon bond length was taken to be 1.45 Å. This is the same as the $C(sp^3)$–$C(sp^2)$ bond length estimated for the open ion, and also the value obtained from an optimization of the energy for protonated ethylene.[55] (This estimated bond length seems very reasonable, since, in the following three-membered cyclic heterocycles, the C–C bond length decreases smoothly with the electronegativity of the heteroatom or group X, *e.g.*, cyclopropane ($X = CH_2$) 1.562 Å, ethylene sulfide (X = S) 1.492 Å, ethyleneimine (X = NH) 1.48 Å, and ethylene oxide (X = 0) 1.467 Å.[52] The electronegativity of Br^+ in the cyclic bromonium ion would be expected to be greater than that of oxygen in ethylene oxide.) However, the extent of rehydridization at the olefinic carbons must be estimated. Thus, while the bond length increases from 1.339 to 1.539 Å from the olefin to the product, 2,3-dibromobutane, the bond angle decreases from the roughly trigonal 123 to the roughly tetrahedral 112.2° (see figures below). A methyl-carbon bond length of 1.52 Å appears reasonable. Methyl–methyl distance calculations were then made for several methyl–carbon–carbon bond angles near 120°. Assuming only a small amount of bond angle change at the transition state (*i.e.*, a methyl–carbon–carbon bond angle of 120°) the methyl–methyl distance is 2.96 Å. An angle of 119° leads to a distance of 2.91 Å. Thus, the calculations again indicate that the steric interactions become more severe at the transition state leading to the bridged ion.



A second approach is based on a comparison of initial olefin and final product geometries. The factors affecting the methyl–methyl distance in the bromonium ion are the central carbon–carbon bond length and the methyl–carbon–carbon bond angle. The geometries estimated for the olefin and the dibromo adduct, given above, are believed to be quite precise. Remembering that no rotation is allowed about the central carbon–carbon bond in a bridged ion, then, if the bond length and bond angle changes from olefin to product occur synchronously and smoothly, the methyl–methyl distance at the transition state (geometry resembling type III) should be somewhere intermediate between that in the olefin (2.995 Å) and the all-cis eclipsed form of the product (2.702 Å).

Finally, an estimate can be made from the known geometries of analogous three-membered-ring heterocyclic systems.[52] Based on the parent molecules ethylene oxide, ethyleneimine, and enthylene sulfide the methyl–methyl distance in the cis-1,2-disubstituted systems can be estimated to be 3.03 (oxide), 2.96

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(52) Tables of Interatomic Distances and Configuration in Molecules and Ions, *Chem. Soc. Spec. Publ. (London)*: No. 11 (1958); No. 18 (1965).

(53) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969); J. E. Williams, V. Buss, and L. C. Allen, *ibid.*, **93**, 6867 (1971).

(54) The methyl–methyl distance in all these calculations refers to the carbon–carbon distance.

(55) D. T. Clark and D. M. J. Lilley, *J. Chem. Soc. D*, 549 (1970).

(imine), and 2.95 Å (sulfide). Thus, if the cyclic bromonium ion geometry resembles these analogous heterocycles, the cis methyl–methyl distance would either be expected to remain roughly the same as that in the olefin, or decrease. Because of the longer bond lengths to the heteroatom and greater distortion of the three-membered-ring system from the equilateral cyclopropane structure, the ethylene sulfide is probably the best model for the cyclic bromonium ion. Therefore, all three methods of estimating its geometry suggest that the steric interactions between *cis*-1,2-methyl groups in a cyclic bromonium ion would either be as severe or, more probably, be increased over those present in the parent olefin.

Kinetics of Thermal Electrocyclic Ring Closure. Alkyl-1,3,5-hexatrienes[1]

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Kinetic studies of thermal electrocyclization of a series of 1- and 3-alkyl-1,3,5-hexatrienes (R = Me, Et, *t*-Bu) yielded the following relative rates: 3-*t*-Bu > 3-Et, 3-Me > 1-Et > 1-Me, H. The activation enthalpies of the 3-alkyl series were, in general, 3 kcal/mol less than either the 1-alkyl counterparts or the parent hydrocarbon. These results can be interpreted in terms of the donative ability of alkyl groups, steric retardation at the reaction sites, and differences in ground-state energies and/or conformation.

Thermal electrocyclic ring closure of various systems containing $4n + 2\ \pi$ electrons has been studied extensively during the past few years.[2,3] However, although the kinetics of isolated examples have been reported,[4-8] no comprehensive study has yet been reported which evaluates the magnitude of substituent effects as a function of chain position.[9] The Woodward–Hoffmann description[2] of this reaction as a disrotatory, concerted process has been confirmed repeatedly in the literature, but primarily in terms of stereochemistry. Few predictions concerning the ability or inability of substituents to affect the course or energetics of this process have been forthcoming, even though an examination of the scattered published examples[3-8] indicates possible substituent participation in the reaction.

In order to demonstrate the existence or absence (and/or magnitude) of substituent effects in the $4n + 2\ \pi$ system, we have studied the thermal ring closure of a series of 1- and 3-alkyl-1,3,5-hexatrienes (alkyl = Me, Et, *i*-Pr, *t*-Bu) in the temperature range 348–423° K, resulting in the formation of 5-alkyl- and 2-alkyl-1,3-cyclohexadienes, respectively, as shown in Scheme I.

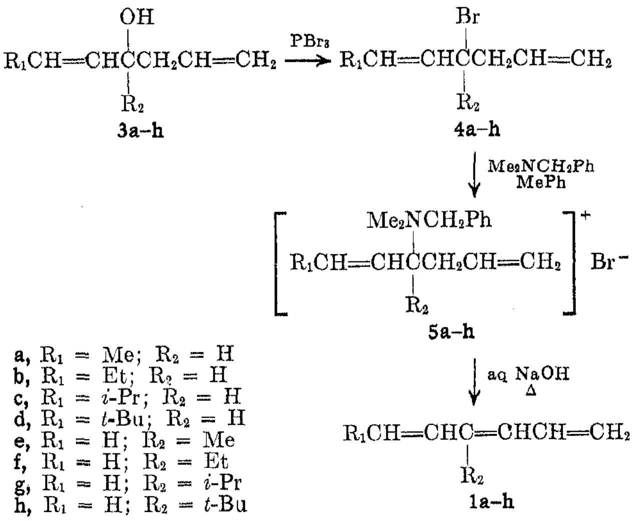
Pure substituted 1,3,5-hexatrienes were prepared from appropriately substituted hexadienols essentially by the method of Hwa, *et al.*,[10] which we have also used previously.[11,12] This is illustrated in Scheme II.

SCHEME I

1 **2**

1a, R_1 = Me; R_2 = H
b, R_1 = Et; R_2 = H
c, R_1 = *i*-Pr; R_2 = H
d, R_1 = *t*-Bu; R_2 = H
e, R_1 = H; R_2 = Me
f, R_1 = H; R_2 = Et
g, R_1 = H; R_2 = *i*-Pr
h, R_1 = H; R_2 = *t*-Bu

SCHEME II



$$R_1CH{=}CH\underset{R_2}{\overset{OH}{C}}CH_2CH{=}CH_2 \xrightarrow{PBr_3} R_1CH{=}CH\underset{R_2}{\overset{Br}{C}}CH_2CH{=}CH_2$$

3a–h **4a–h**

$$\Big\downarrow \text{Me}_2\text{NCH}_2\text{Ph}\ \text{MePh}$$

$$\left[R_1CH{=}CH\underset{R_2}{\overset{Me_2\overset{+}{N}CH_2Ph}{C}}CH_2CH{=}CH_2\right]^{+} Br^{-}$$

5a–h

$$\Big\downarrow \text{aq NaOH}\ \Delta$$

$$R_1CH{=}CH\underset{R_2}{C}{=}CHCH{=}CH_2$$

1a–h

a, R_1 = Me; R_2 = H
b, R_1 = Et; R_2 = H
c, R_1 = *i*-Pr; R_2 = H
d, R_1 = *t*-Bu; R_2 = H
e, R_1 = H; R_2 = Me
f, R_1 = H; R_2 = Et
g, R_1 = H; R_2 = *i*-Pr
h, R_1 = H; R_2 = *t*-Bu

The trienes were obtained free of contamination from either the ring-closure products (**2a–h**) or the corresponding aromatized products. In general, a mixture of geometric isomers may be expected from the Hwa procedure; however, as can be seen in Table I, several trienes were obtained geometrically pure.

It is obvious that the 1-*i*-Pr and 1-*t*-Bu trienes thus could not be included in the kinetic analysis. We have not been able to synthesize these trienes with a cis configuration about the central double bond.

The trends evident in the two series can be rationalized from consideration of the most probable ground-

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[1] (a) Portions of this paper were presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972. (b) Taken in part from the Ph.D. dissertation of Thor P. Jondahl, Northern Illinois University, Dec 1971.

[2] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie-Academic Press, Weinheim/Bergstr., 1970.

[3] H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

[4] K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964).

[5] E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Lett.*, 385 (1965).

[6] K. W. Egger, *Helv. Chim. Acta*, **51**, 422 (1968).

[7] E. Vogel, W. Grimme, and E. Dinné, *Tetrahedron Lett.*, 391 (1965).

[8] C. J. Gaasbeek, H. Hogeueen, and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **91**, 821 (1972).

[9] The present discussion applies only to acyclic examples. The authors are aware of the many cyclic examples, but do not feel that their inclusion would be meaningful in that the complication of ring size and conformation obscures the presence or absence of steric and other secondary effects.

[10] J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *J. Amer. Chem. Soc.*, **82**, 2537 (1960).

[11] C. W. Spangler and G. F. Woods, *J. Org. Chem.*, **28**, 2245 (1963).

[12] C. W. Spangler and G. F. Woods, *ibid.*, **30**, 2218 (1965).