with base. The spectrum of citramalic acid (**8**) appeared which also was evident in the previous run in small amounts (methyl, 1.48; nonequivalent methylene, 2.41, 2.77 ppm). This spectrum was very similar to that of authentic material (Aldrich).

Product Identification Runs.—Citraconic acid (0.302 g) plus potassium carbonate (320 mg) was heated briefly in deuterium oxide (1.0 ml) plus 10 mg of tetramethylammonium bromide. Bromine was added in small amounts with intermittent cooling. An aliquot was taken and checked by nmr which showed the absorptions of **12**, δ 1.74, 5.71 (53%); unreacted starting material, (21%); **9** and **10** δ *ca.* 1.92 (16%), **13** and **14**, δ 1.38 and 1.31, respectively (10%). The spectrum was rerun at intervals, eventually forming **9** and **10** (38%), **13** and **14** (12%), and **16** (28%).

In another run on large scale the intermediate **12** was carefully treated with HCl in the cold, to pH 2. An oil slowly separated (*ca.* 3.5 g from 10 g of starting material). The infrared spectrum showed a strong absorption at 1860 cm^{-1} plus the carboxylic absorption at 1720 (broad). The nmr of this material showed the material to be 25% of the lactone **12**, 30% **9**, and 45% of a material very similar to **2**. If HBr were used for acidification, the latter gave a spectrum identical with authentic **2**.

In another run, the lactone **12** was formed similarly, then treated with excess potassium carbonate. The spectrum of **12** diminished rapidly and was replaced by the bromohydrin **14** and acetocetic acid (**16**), δ 2.25 (three protons) and 3.47 (two protons). The final solution showed 30% **14**, 13% **13**, and 26% **10**. This solution was basified with potassium hydroxide to pH 13. The bromohydrin changed in large part to **16**, but a new peak appeared δ 1.58, believed to be the epoxide **18**.

The bromohydrin **14** was also produced by treatment of citraconic acid (10.0 g) with N-bromosuccinimide (14.4 g) stirred in 20 ml of H_2O overnight with 0.1 ml of sulfuric acid. The aqueous solution was mixed with 20 g of ammonium chloride and repeatedly extracted with ether. The organic layers were dried over $MgSO_4$, evaporated, and checked by nmr. The product, 5.0 g, was *ca.* 70% **9** and 30% **14**.

Mesaconic acid (320 mg) was treated with potassium carbonate in deuterium oxide until the pH was *ca.* 6.5. Bromine was added dropwise with intermittent cooling. The nmr showed the following absorptions, in addition to **20** (20%), **14** (17%), **13** (8%), unidentified peak δ 1.66 (4%), unreacted mesaconic (11%), unidentified peak δ 2.08 (4%), and **16** (12%) were produced.

Upon acidification with hydrobromic acid **20** rather slowly formed **14**, then **13**. No more than a small quantity of **3** was formed, by comparison of spectra before and after addition of authentic **3**.

In another run **20** was formed as before, then treated with potassium carbonate; **14**, **13**, and **16** were again the major products similar to the experiments with **12**.

To check that **12** and **20** produced the same bromohydrin **14**, 1.0 g of citraconic acid and 1.4 g of mesaconic acid were treated with Br_2 in a neutral, aqueous solution, forming **12** and **20**; upon treatment with K_2CO_3 only a single absorption due to **14** and a single absorption due to **13** was apparent in addition to **16**.

To test for propionaldehyde, **2** or **3** (10.0 g) was added to 50 ml of water plus an equimolar amount of potassium carbonate at *ca.* 80° (steam bath). Two traps were used, one filled with ice, the other with Dry Ice–acetone. Nitrogen was passed through the reaction mixture for *ca.* 30 min. The ice trap contents were analyzed by nmr and vpc and showed water and traces of organic material. The Dry Ice trap contents showed about 1 ml of a liquid, mainly water in the case of **2** with about 20% of an equal mixture of acetone and propionaldehyde. In the case of **3** the trapped material (*ca.* 1 ml) showed equal quantities of water and organic material of which there was 60% propionaldehyde and 40% acetone.

The rate solutions were prepared in volumetric flasks to which *ca.* 20 ml of redistilled water, 200 mg of substrate, and the requisite amount of sodium acetate had been added. This mixture was allowed to come to temperature. The rate was begun by addition of a twofold molar equiv of standard sodium hydroxide, which also had been equilibrated. The evolution of bromide was followed by adding 5-ml aliquots to cooled, pretitrated solutions of standard silver nitrate and sodium thiosulfate. The titration was rapidly completed after addition. Rate constants and activation parameters were calculated by standard procedures.[28]

Registry No.—**7**, 16520-64-2; **9**, 16503-84-7; **10**, 16503-85-8; **11**, 67-64-1; **12**, 16503-86-9; **13**, 16503-87-0; **14**, 16520-63-1; **16**, 141-81-1; **18**, 16503-89-2; **20**, 16503-86-9; **21**, 16503-91-6; **22**, 16503-83-6.

Acknowledgment.—This work was begun at Iowa State University and was supported in part by National Science Foundation Grant GP6765. Permission by ISU to use equipment purchased with this grant is gratefully acknowledged.

[28] B. Stevens, "Chemical Kinetics," Chapman and Hall, London, 1961, pp 17, 37.

Conformational Preferences in Diastereomers. IV. 1,2,3 Diastereomers

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The four diastereomers of the 1,2-dibromo-1,3-diphenylbutane system and two of the three diastereomers in the 1,2,3-tribromo-1,3-diphenylpropane system are assigned relative configurations on the basis of nmr studies in deuteriochloroform, dipole moment, and stereospecific reaction data. Iodide-catalyzed debrominations proved to be nonstereospecific. The *erythro* dibromide centers in the former system are nearly conformationally pure, whereas the *threo* centers here conformationally mixed. In the latter system the reverse is true. The results are discussed in terms of possible unfavorability of *gauche* bromine interactions. The importance of 1,3 eclipsing interactions is emphasized. The mechanistic implication of the bromination product yields from the isomeric 1,3-diphenylbutenes is discussed in terms of possible bromonium ions.

The use of nuclear magnetic resonance spectra to aid in the assignment of configurations of acyclic molecules has found increasing application in recent years.[1-8] Most frequently use is made of the Karplus relationship[9,10] which suggests that predominantly *trans* vicinal protons will exhibit large coupling constants (J) in the vicinity of 11–13 cps, whereas predominantly *gauche* protons show low J values of *ca.* 1–3 cps.

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[1] J. Canceill, J. Basselier, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1906 (1963).

[2] M. Barbieux and R. Martin, *Tetrahedron Lett.*, 2919 (1965).

[3] M. Stiles, R. Winkler, Y. Chang, and L. Traynor, *J. Amer. Chem. Soc.*, **86**, 3337 (1964).

[4] R. C. Fahey, *ibid.*, **88**, 4611 (1966).

[5] M. Dewar and R. Fahey, *ibid.*, **85**, 3645 (1963).

[6] G. J. Karabatsos and N. Hsi, *ibid.*, **87**, 2864 (1965).

[7] A. Bothner-By and D. Jung, *ibid.*, **86**, 4025 (1964).

[8] S. Brownstein, *Can. J. Chem.*, **39**, 1677 (1961).

[9] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

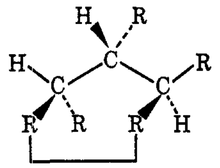
[10] H. Gutowsky, *J. Chem. Phys.*, **38**, 3353 (1962).

In studies of simple diastereomers,[11] the *erythro* isomer frequently has a larger coupling constant than the *threo* isomer (the definition of "*erythro*" being based on the size of the groups). The *erythro* isomer thus has a larger population of a rotomer with *trans* protons. This generalization is not to be expected when strong intramolecular hydrogen bonding is possible,[1,12,13] and possibly not when extreme steric hindrance is present,[4,11,14,15] such as in compounds with *t*-butyl substituents.

Earlier work[15–19] has emphasized the importance of 1,3 interactions between sizable groups, as well as 1,2 (*i.e.*, *gauche*) interactions as factors which determine conformational preferences in diastereomers.

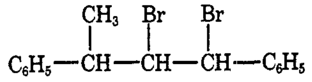
It appeared desirable to move to the more complex system of diastereomers which involve three asymmetric centers. The simpler systems suffer from the difficulty that the two rotomers with *gauche* protons are not distinguishable since both have similar, low J values.

In the system of 1,2,3 diastereomers, one *gauche* H–H rotomer is prohibited by 1,3 repulsions. Thus if the nmr spectrum exhibits a low coupling constant for a given set of protons, the rotomer can be specifically identified.



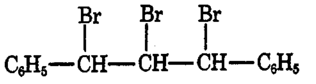
improbable *gauche* rotomer

The major system of interest in this study is 1,2-dibromo-1,3-diphenylbutane, **1**, studied earlier by Stoermer and Kootz.[20] The system 1,2,3-tribromo-1,3-diphenylpropane, **2**, will be briefly considered.



$$C_6H_5-\overset{CH_3}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-C_6H_5$$

1



$$C_6H_5-\overset{Br}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-C_6H_5$$

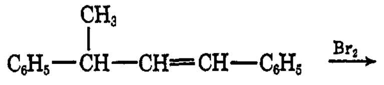
2

The system **1** has three asymmetric centers and a total of four possible diastereomers. The system **2** has two *meso* and a single DL diastereomer.

It is the object of this study (i) to attempt to elucidate the configuration at the three asymmetric centers of **1**, (ii) to attempt to arrive at some meaningful conclusion about the conformational preferences in these complex systems, and (iii) to elucidate the modes of attack of bromine upon the parent olefin yielding the diastereomers of formula **1**.

Results and Discussion

Analysis of Configuration.—Addition of bromine to either *cis*- or *trans*-1,3-diphenyl-1-butene, **3**, yielded four diastereomers. Three of these were obtained crystalline in agreement with Stoermer and Kootz,[20] and will be identified by melting point for the present. The fourth diastereomer was an oil, somewhat impure by a mixture with **4** and **5**, which defied all attempted means of purification. The resonance absorptions of the oil, **7**, fortunately were fairly well separated from its impurities, **4** and **5**, and the coupling constants and chemical shifts could be accurately determined. These data for **7** as well as similar data for **4**, **5** and **6** are listed in Table I.



$$C_6H_5-\overset{CH_3}{\overset{|}{CH}}-CH{=}CH-C_6H_5 \xrightarrow{Br_2}$$

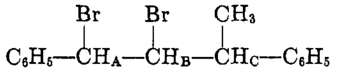
3

4 + **5** + **6** + **7**

mp 128° mp 122° mp 80° oil

TABLE I

NMR COUPLING CONSTANTS, CHEMICAL SHIFTS AND DIPOLE MOMENTS FOR DIASTEREOMERS **4–7**



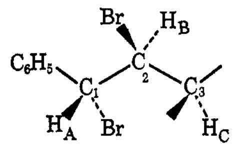
$$C_6H_5-\overset{Br}{\overset{|}{C}}H_A-\overset{Br}{\overset{|}{C}}H_B-\overset{CH_3}{\overset{|}{C}}H_C-C_6H_5$$

Diastereomer	Assignment[a]	Mp, °C	J_{AB}	J_{BC}	Chemical shifts[b]			Dipole moment[c]
					H_A	H_B	H_C	
4	EE	128	11.6	3.0	4.64	4.78	4.00	1.30
5	ET	122	11.1	2.8	5.15	4.71	3.90	1.20
6	TE	78	4.2	8.2	4.90	4.30	3.15	2.55
7	TT	Oil	6.2	6.2	5.15	4.50	3.20	. . .

[a] Justification for this assignment of configuration is given in the Discussion. [b] Approximately 10–15% solutions in $CDCl_3$ using tetramethylsilane as an internal standard taken as 0 ppm. Spectra taken on a Varian A-60 instrument. [c] These data are considered good ±0.20; these data have duplicated the spectrum, by computer simulation.

It is apparent from the coupling constant data that **4** and **5** are characterized by strong conformational preferences involving predominately *trans* A and B protons and *gauche* B and C protons.

The dipole moment data are not as definitive as other data;[21] however, a tentative conclusion may be made. The major contributor to the resultant moment is the bromine (group moment 1.7 D) although the phenyl group is also a fairly strong contributor (group moment 0.8–1.2 D). The resultant moment for **6**, 2.55 D, is fairly close to other examples thought to contain *gauche* bromines.[15,22] The somewhat lower values **4** and **5** are taken as probably indicative of *trans* bromines with the major contributor to the resultant being the phenyl groups. The similarity of the dipole moments for **4** and **5** probably indicates similar orientation of the halogens. A tentative assignment of the configuration for **4** and **5** at carbons 1 and 2 may



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[11] (a) C. A. Kingsbury and W. Thornton, *J. Org. Chem.*, **31**, 1000 (1965); (b) C. A. Kingsbury and W. Oliver, unpublished results.

[12] J. B. Hyne, *Can. J. Chem.*, **38**, 125 (1966).

[13] J. Huffman and R. P. Elliott, *J. Org. Chem.*, **30**, 365 (1965).

[14] See, however, G. Whitesides, J. P. Sevenair, and R. Goetz, *J. Amer. Chem. Soc.*, **89**, 1135 (1967).

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

[16] C. G. Overberger and T. Kurtz, *ibid.*, **31**, 388 (1966).

[17] Y. Fujimara and S. Fujiwara, *Bull. Chem. Soc. Jap.*, **37**, 1005 (1964).

[18] D. Doskocilova and B. Schneider, *Collect. Czech. Chem. Commun.*, **29**, 2290 (1964).

[19] T. Shimanouchi and T. Tasumi, *Spectrochim. Acta*, **17**, 755 (1961).

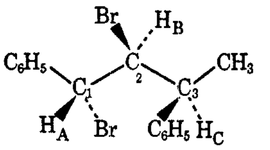
[20] R. Stoermer and B. Kootz, *Chem. Ber.*, **58**, 2613 (1928).

[21] L. O. Smith and S. J. Cristol, "Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1966, pp 679, 681.

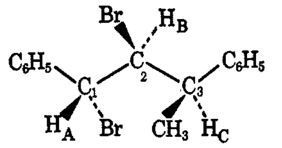
[22] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, p 206.

now be made. *trans* bromines and *trans* protons A and B define the *erythro* configuration at C-1,2. Compounds **4** and **5** then differ at C-3. If **4** and **5** are *erythro* at C-1,2, then **6** and **7** are *threo*.

Consideration of the chemical shift data for H_A permits a decision concerning configuration at C-2 and C-3. In one diastereomer, models show H_A is opposite the face of a phenyl group at C-3. In the other diastereomer it is opposed to a methyl group. The former diastereomer should exhibit H_A far upfield from the latter diastereomer. The data in Table I show **4** has the upfield proton H_A. Complete configurations are assigned as shown. Configurations of **4** then are *erythro* at C-1,2 and *erythro* at C-2,3, hereafter called EE. Configuration of **5** is ET.



4, EE_1

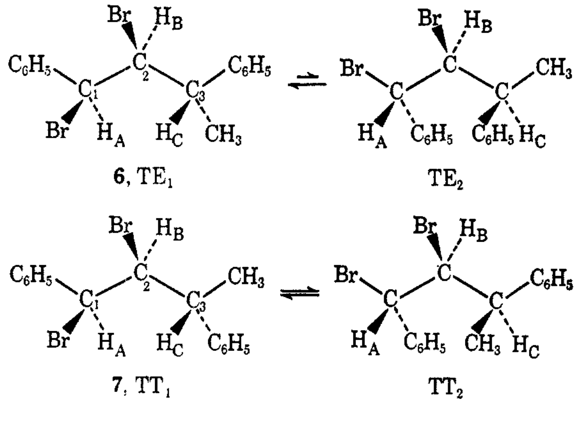


5, ET_1

Compounds **4** and **5** provide one more example of the alternation of coupling constants in a three-center system.[15] If J_{AB} is large, J_{BC} will invariably be small and *vice versa* (compare compound **6**). This arrangement allows 1,3 interactions between sizeable groups to be minimized as discussed earlier.[23,24] If J_{AB} and J_{BC} were either both large or both small a severe 1,3 interaction between sizeable groups would result.

A decision concerning configurations at C-2 and C-3 is much less secure for **6** and **7** since these compounds are not conformationally pure and chemical shift data are the result of an average of at least two conformations. A tentative assignment is given in Scheme I for reasons brought out below.

Scheme I



The coupling constant data show TE_1 is more important than TE_2 ($J_{AB} = 4.2$, $J_{BC} = 8.2$) whereas TT_1 and TT_2 have equal weight ($J_{AB} = J_{BC}$). Examination of Stuart–Breigleb models shows a possible reason for this difference. The models clearly show that TE_1 is more stable than TE_2 due to steric interference of the phenyls at C-1 and C-3 in the latter. Even though one phenyl is canted downward and the other upward, the *ortho* positions interfere with one another severely. On this basis the most conformationally pure diastereomer, **6**, mp 80°, is assigned the TE configuration, and **7** the TT configuration. These assignments are also consistent with the usual observation that the *erythro* centers exhibit the larger *J* values.

Unfortunately, consideration of the chemical shift data leads one to the opposite conclusion. In TE_1 neither H_A or H_C is opposed to a phenyl, whereas in TT_1 and TT_2 the same protons are opposed to a phenyl at least part of the time. Diastereomer **7** should exhibit upfield absorptions compared to **6**, which is not the case, although the difference is small. Attempts to account for the chemical shifts of a given proton in terms of a preferred conformation of the phenyl group at the same carbon were unsuccessful.

Additional data on the bromination yields will be given later. These data are best interpreted in terms of the configurations given above.

It had been hoped that additional data concerning configuration could be obtained from debromination experiments. However, iodide-catalyzed debromination[25] in methanol proved to be stereoselective rather than stereospecific. All four diastereomers yield predominately the most stable olefin, *trans* **3**. The data are recorded in Table II. It is noteworthy that the most *cis* isomer observed was with diastereomers **6** and **7** thought to possess the *threo* configuration at C-1,2. Nevertheless, the major reaction of **6** and **7** was unexpectedly an over-all *cis* debromination. Control experiments proved no isomerization of *cis* to *trans* olefins was important under the reaction conditions. These results were similar to the zinc-catalyzed debromination experiments of Stoermer and Kootz.

Table II

Per Cent *trans* of a *cis–trans* Mixture of **3** Resulting from Reaction of **4–7** in CH_3OH with KI

	4	**5**	**6**	**7**
trans, %	100	100	87	67[a]

[a] Corrected for contribution of impurities **4** and **5**.

Similar experiments[26] on authentic *threo*-1,2-dibromo-1-phenyl-3-methylbutane likewise yielded predominately *trans*-1-phenyl-3-methyl-1-butene.

A reaction course involving a preliminary S_N2 by iodide, then rapid dehalogenation by iodide,[27] does not seem likely in view of the steric hindrance of the substrate.

In our experience[26] nonstereospecific debrominations are frequently observed in diastereomers containing benzylic halogens. A carbonium ion mechanism as shown in Scheme II seems attractive. The intermediate carbonium ion is presumed to be sufficiently long lived to achieve rotational equilibrium.

Conformational Preferences.—An interesting point brought out previously is that the C-1,2 *erythro* isomers **4** and **5** are nearly conformationally pure, whereas the *threo* isomers involve equilibria between at least two conformers. From molecular models the following

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(23) E. J. Corey and R. B. Mitra, *J. Amer. Chem. Soc.*, **84**, 2938 (1962).

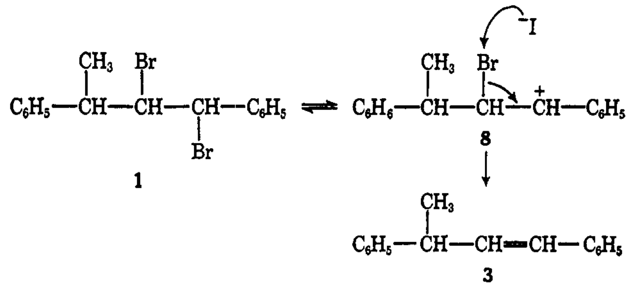
(24) D. J. Millen, "Progress in Stereochemistry," Vol. III, W. Klyne, Ed., Butterworth and Co. Ltd., London, England, 1962, p 158.

(25) S. Winstein, D. Pressman, and W. G. Young, *J. Amer. Chem. Soc.*, **61**, 1645 (1939).

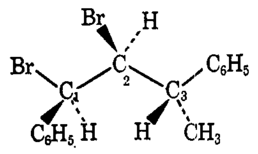
(26) Experiments performed by Mr. Gary Underwood.

(27) (a) See, however, H. L. Goering and H. Espy, *J. Amer. Chem. Soc.*, **77**, 5023 (1955); (b) W. M. Schubert, H. Steadly, and B. S. Rabinovitch, *ibid.*, **77**, 5755 (1955).

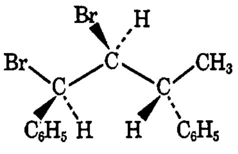
SCHEME II



forms of **4** and **5** (called EE_2 and ET_2) also seem quite stable. Severe 1,3 interactions are not significantly different in EE_1 and EE_2 of **4** although the 1,3 phenyl interactions would seem to make ET_2 less somewhat stable than ET_1 of **5**. The question is then, what forces or interactions impose rigidity on **4** and **5** but not on **6** and **7**.



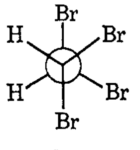
4, EE_2



5, ET_2

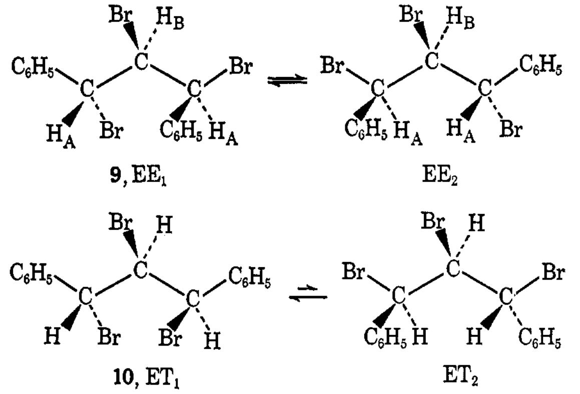
If one accepts the fact that 1,3 interactions are potent factors in determining conformations, the only possible conformations are TE_1 and TE_2 and TT_1 and TT_2 for **6** and **7** shown in Scheme I. Each of these involves *gauche* Br–Br interactions. The experimentally observed conformation for **4** is EE_1 and for **5** is ET_1, neither of which involves *gauche* bromines. The possible, but not observed, conformations EE_2 and ET_2 both involve such interactions. It is possible that such interactions are energetically unfavorable and this factor dominates the choice of conformation in **4** and **5**. Where such interactions are unavoidable in either conformer as in **6** and **7**, both conformers are populated. By a rough calculation the dipole–dipole repulsion of *gauche* bromines is on the order of 1 kcal. Polarization interactions of the two bromines may provide a slight counteracting attractive force.

We are hesitant to ascribe a dominating influence totally to this factor, however. In other studies, vicinal halogens showed no overwhelming disposition to be *trans*.[15,26,28,29] Of particular interest is the infrared study of tetrabromoethane which showed the totally *gauche* conformation to be highly populated in solution, although *trans* bromines were evident in part in dibromoethane (dependent upon the experimental conditions).[24]



It is perhaps instructive now to consider the second set of diastereomers **2**.[30] Only two of the three diastereomers were obtained; the first, **9**, mp 182°, is thought to be one of the *meso* structures, specifically the EE diastereomer, whereas the second, **10**, mp 138°, is assigned the DL structure (ET or TE) based on data given in the Experimental Section. The spectrum of **9** is a classic A_2B case[31] with J_{AB} *ca.* 6.3 cps ($CDCl_3$). It is not thought that A protons are equivalent in a given conformer, but that rapid interconversion of two equivalent mirror image structures exists (Scheme III).

SCHEME III



On the other hand, the DL compound, **10**, is strongly held in a single conformation thought to be ET_1 (Scheme III). The spectrum of **10** is an AMX, with J_{AM} = 1.9 cps, and J_{MX} = 10.9 cps. These data are consistent with either ET_1 or ET_2; however, the far downfield chemical shifts of A, 6.13 ppm, and X, 5.35 ppm (in $CDCl_3$), are much more consistent with ET_1 (*cf.*, the differences between **5** and **6**). Molecular models likewise show ET_1 to be the least sterically crowded. The dipole moment of **10**, 1.9 D, similarly is more consistent with the ET_1 structure.

If ET_1 is indeed the dominant rotomer, the same reasoning can be applied as with **4–7**. The rotomer ET_1 involves a single *gauche* Br–Br interaction whereas the presumably less stable ET_2 involves two such interactions.

A second factor should perhaps be mentioned as a possible reason for the stability of certain rotomers over others. Certain types of 1,3 interactions may be attractive rather than repulsive, particularly where atoms of dissimilar electronegativity are involved. It can be seen that the stable rotomers frequently involve 1,3 interactions between bromines and protons. Two exceptions to this generalization exist; the apparent equivalent stability of TT_1 and TT_2 of **7** being the most serious of this study. Similar ideas have been proposed in studies of bromocyclohexanes.[32]

Bromination Studies.—Bromination of either *cis* or *trans* olefin **3** produced all four diastereomers **4–7** in unequal yields. The data are recorded in Table III. Beginning with highly reactive *cis* isomer, the yield of the TT isomer **7** is much larger than from *trans* **3**. The reverse is true for the yields of EE **4**.

Initial attack of the brominating species very likely occurs at C-2, and the resulting benzylic ion for the present is assumed to be an open ion.[33] The initial mode of attack determines stereochemistry at C-2,3. The situation is the most clear for the *cis* isomer which

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[28] N. Sheppard, *Advan. Spectrosc.*, **1**, 295 (1959).

[29] R. E. Kagarise, *J. Chem. Phys.*, **24**, 300 (1956).

[30] R. Lespieau and R. Wakeman, *Bull. Soc. Chim. Fr.*, **51**, 384 (1932).

[31] The authors thank Dr. R. W. King for elucidation of the spectrum and interpretation of its significance.

[32] E. Eliel and R. Haber, *J. Amer. Chem. Soc.*, **81**, 1249 (1958).

[33] (a) M. L. Poutsma, *ibid.*, **87**, 4293 (1965), and earlier papers; (b) R. Fahey and C. Shubert, *ibid.*, **87**, 5172 (1965).

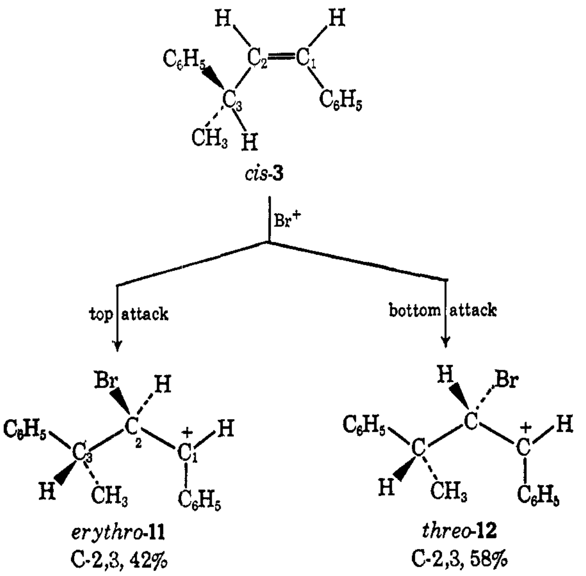
Table III
Relative Yields of Diastereomers 4–7 from *cis* and *trans* 3

Alkene **3**	Diastereomeric yield,[a] %			
	4, EE	**5**, ET	**6**, TE	**7**, TT
cis[b]	17	41	25	17
trans[c]	40	39	17	5

[a] Determined by integration of expanded nmr spectrum. The yields are considered good to ±4%. [b] Brominated in CCl_4 solution at 0°C, protected from light. [c] Brominated in CS_2 solution at 0° in diffuse light.

is nearly conformationally pure, as shown by the large methine–vinyl *J* value (11 cps) indicative of *trans* protons (the methine proton is eclipsed with the double bond). The less sterically hindered *trans* isomer may accommodate other groups[34] eclipsed with the double bond. The stereochemistry of attack is illustrated in Scheme IV. As shown, top attack, where the brominating species enters over the phenyl, yields the *erythro* isomer in 42% yield (sum of **4** and **6**), whereas a somewhat preferred attack over methyl yields the *threo* isomer in 58% yield. The difference in yields is not large, but it is consistent with this model. Attack on an unsaturated center next to an asymmetric center is also the basis of the very successful Cram rule,[35] from which predictions are made using a conformation of the aldehyde or ketone other than the most stable.[36]

Scheme IV

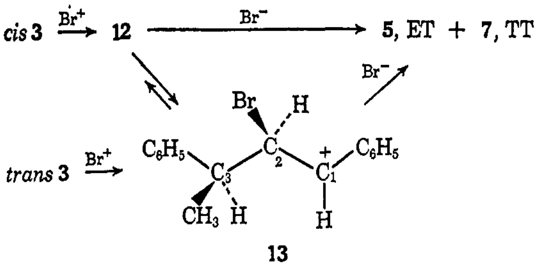


Initial attack on *trans* **3** yields 56% *erythro* at C-2,3. Predominant attack over hydrogen on a conformation with methyl eclipsed with the double bond seems attractive. If the hydrogen were eclipsed with the double bond, the *threo* isomer would probably again predominate. Again the differences are not large.

Completion of the reaction sequence involves attack of the bromide at C-1 after varying amounts of internal rotation have occurred. This attack determines stereochemistry at C-1,2. Hindrance to approach of the bromide by substituents at C-2 and C-3 must be considered. It is of interest to know which dominates.

The intermediate ion or ions of *threo* configuration at C-2,3 will be considered first. The total yield of products of *erythro* configuration at C-1,2 (**5**) is larger than the *threo* (**7**). Furthermore, the yields are rather similar beginning with either the *cis* olefin **3** (71% **5**, 29% **7**) or the *trans* olefin **3** (89% **5**, 11% **7**). It seems likely that a common intermediate exists in the bromination of either *cis* or *trans* **3** as shown in Scheme V. Very likely the highly hindered ion **12** formed initially from *cis* **3** rotates about the C-1,2 bond to form the more stable structure **13** (the conformer shown appears to be the most stable from Stuart–Breigleb models). Some capture of **12** by bromide occurs so that the relative yields of **5** and **7** are not quite the same as from *trans* **3**.

Scheme V

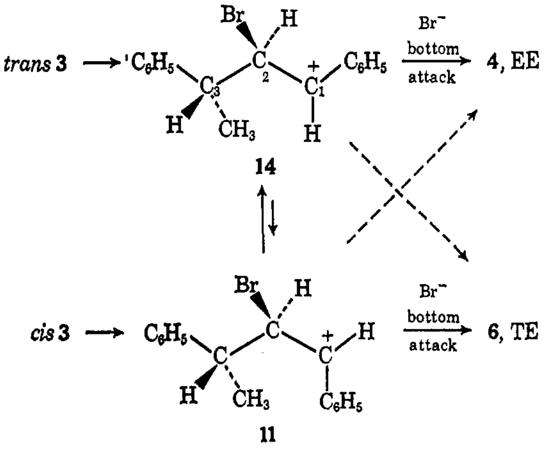


It is noteworthy that the predominant mode of attack by bromide on **13** is from the opposite side of the molecule from the bromine at C-2, to yield the *erythro* isomer **5**. Whether or not there is bridging by the bromine at C-2 is not answerable from the data of this study, but it seems likely that bromine does bridge in part.

The intermediate ion or ions of the *erythro* configuration at C-2,3 behave rather differently depending upon their origin. Thus product of *threo* configuration at C-1,2 (**6**) predominates (60% **6**, 40% **4**) where *cis* **3** is the starting material, whereas the *erythro* product predominates from the *trans* isomer (30% **6**, 70% **4**).

The interpretation of the results is perhaps more straightforward beginning with *trans* **3** (Scheme VI). Initial attack of Br^+ yields the sterically unhindered

Scheme VI



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[34] A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Amer. Chem. Soc.*, **84**, 2742 (1962).

[35] D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952).

[36] E. Eliel, N. Allinger, S. Angyal, and G. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p 34.

ion **14**. Again the bromine at C-2 may form the bridged species in part. The predominant products again results from bromide attack remote from the bromine at C-2 to yield **4**.

Beginning with *cis* **3**, the ion **11** is formed, which shows severe steric crowding. Some internal rotation about the C-1,2 bond occurs giving **14**. The ion **14** would then yield the same product ratio as that observed from *trans* **3**. From models, this rotation seems rather difficult and involves the breaking of overlap between the p orbital at C-1 and the aromatic group.

The predominate pathway is attack of bromide directly on **11**. Again attack occurs predominantly on the side of the molecule remote from the bromine at C-2 yielding the *threo* isomer **6**.

The difference between the reaction model shown in Scheme V and that in Scheme VI is that extensive internal rotation occurs in the former case but not in the latter.[37]

The primary conclusion from the above data is that a bromine substituent at C-2 is dominant over a phenyl or methyl at C-3 in its effect on bromide attack at C-1.

Experimental Section

1,3-Diphenyl-1-butenes.—To a solution of 26.8 g (0.2 mol) of 2-phenylpropanol (Aldrich Chemical Co., Inc.) and 77.6 g (0.2 mol) of triphenylbenzylphosphonium chloride in 500 ml of commercial absolute ethanol was added dropwise, under nitrogen, 1 l. at 0.2 *M* lithium ethoxide. After the addition was complete, the reaction was stirred for an additional 24 hr at room temperature. Sufficient water was added to give a 60% ethanol solution and the entire mixture was poured into a large separatory funnel. The dark brown oil which separated was collected and washed two times with 50-ml portions of 60% ethanol and then dried over Molecular Sieve (Linde 4A). The crude mixture of *cis* and *trans* olefins was separated by distillation through an 18-in. spinning band column at reduced pressure (*ca.* 2 mm). Twenty-four 2-cc fractions were collected and analyzed by vapor phase chromatography using a 0.25 in. × 8 ft QF_1 column (5% QF_1 on 60–80 mesh HMDS treated Chromosorb W) at a column temperature of 195° using a 65 cc/mm helium flow. The retention times of *cis* and *trans* were 3 and 4.5 min, respectively. Fractions 2–10, bp 109–112° (2 mm), were *cis* **3** of 99% purity, fractions 11–14 were a mixture of *cis* and *trans* **3** and fractions 15–24 were *trans* **3** of 99% purity. The nmr spectral data for the olefins are identical with those reported by Ela and Cram.[38]

Triphenylbenzylphosphonium Chloride.—To a solution of 100 g (0.382 mol) of triphenylphosphine (Aldrich Chemical Co., Inc.) in 250 ml of xylene was added 48.59 g (0.38 mol) of benzyl chloride. The reaction mixture was stirred at reflux temperature overnight. The white salt was filtered, washed with pentane, and dried in an oven at 60°, yield 128 g (86.5%).

Bromination of *cis* 3.—A solution of 10 g (0.027 mol) of the olefin in 50 cc of carbon tetrachloride was cooled to 0°. The reaction flask was wrapped in aluminum foil and a solution of 4.4 g (0.0275 mol) of bromine in 20 ml of carbon tetrachloride was added dropwise. After the addition was complete (30 min), the reaction mixture was stirred for an additional 60 min and then poured over ice and extracted with carbon tetrachloride. The carbon tetrachloride layer was washed with dilute sodium bisulfite, water, and then dried over anhydrous magnesium sulfate. A small amount of the carbon tetrachloride solution was concentrated by rotary evaporation at room temperature. The resulting residue was dissolved in deuteriochloroform and an nmr spectrum was recorded. The portion of the spectrum from 220 to 320 cps was again recorded using a 100-cps sweep width. Integration over this expansion allowed calculation of yield of each diastereomer.

The carbon tetrachloride was removed from the major portion of the crude product by rotary evaporation and the residue crystallized upon standing. The crystals (crop A) were collected and the residual oil was allowed to stand. After several days the oil crystallized in large plates, mp 61–67°. The crystals were taken up in fresh CCl_4 and pentane was added. The first crystals to separate were filtered off and the mother liquor was cooled yielding dibromide **6**, mp 78–80° (lit.[20] mp 78–80°).

Dibromide (**5**), mp 122–123° (lit.[20] mp 122°), was obtained by dissolving crop A in a suitable volume of solvent prepared by mixing 100 ml of ethanol with 50 ml of ethyl acetate and 25 ml of water. After four recrystallizations from this solvent the pure dibromide was obtained.

Dibromide **7** was not obtained free from diastereomeric impurities; however, a mixture of dibromide **4**, **5**, and **7** was obtained by repeated fractional recrystallization. This mixture contained 34% dibromide (**7**), 28% dibromide (**4**), and 38% dibromide (**5**) *via* nmr integration. Dibromide (**4**) is most easily obtained from the product mixture derived from bromination of *trans* olefin.

Bromination of *trans* 3.—A solution of 4.4 g of bromine in 25 ml of carbon disulfide was added dropwise to a solution of 10 g (0.027 mol) of the olefin in 50 ml of carbon disulfide. The reaction mixture was stirred at 0° for 2 hr and then allowed to warm to room temperature. The carbon disulfide was removed by rotary evaporation at room temperature and the residue was dissolved in carbon tetrachloride and again stripped of solvent. The crude product was taken up in fresh carbon tetrachloride and washed with sodum bisulfite, water, and then dried over magnesium sulfate. A small portion of the carbon tetrachloride solution was concentrated and the residue was dissolved in deuteriochloroform and an nmr spectrum was recorded. The portion of the spectrum from 220 to 320 cps was again recorded using a 100-cps sweep width. Integration over this expansion allowed calculation of yield of each diastereomer.

After removal of the solvent from the bulk of the product, the residue was dissolved in a large excess of ethanol and allowed to stand at room temperature. Long needles of the pure dibromide **4**, mp 128–129° (lit.[29] 128–129°),[20] separated after several hours.

Dipole Moments.—The technique of dipole moment measurement has been discussed previously.[15] Cyclohexane was the usual solvent. The nmr spectra of the diastereomers were also determined in cyclohexane to be sure no large change in conformation resulted form change in solvent from deuteriochloroform to cyclohexane. These data are **5**, J_{AB} = 10.8 cps, J_{BC} = 2.7 cps; **6**, J_{AB} = 3.5 cps, J_{BC} = 8.5 cps; and **7**, J_{AB} = 6.4 cps, J_{BC} = 6.4 cps.

Elimination Procedure.—A solution of 1 g of potassium iodide in 50 ml of commercial absolute methanol was prepared and 5 ml of this solution was pipetted into a test tube containing 0.10 g of the dibromide. The tubes were sealed and placed in a bath at 60° for 85 hr. The tubes were cooled to room temperature, broken and the contents poured over ice. The reaction mixture was extracted with ether and the ether layer was washed with cold, dilute sodium thiosulfate, water, and then dried over anhydrous magnesium sulfate. The ether was removed by distillation and the residue was analyzed by vpc using the QF_1 column previously described. The results are given in Table II.

***cis-trans* Isomerization of 3.**—A solution of 0.05 g of iodine, 0.1 g of potassium iodide, and 0.1 g of *cis* **3** in 5 ml of commercial absolute methanol was placed in a test tube. The tube was sealed and maintained at 60° for 160 hr. No *trans* olefin could be detected in the reaction mixture by vpc analysis.

1,2,3-Tribromo-1,3-diphenylpropanes were prepared similar to the method of Lespieau and Wakeman,[30] by addition of excess bromine in carbon disulfide to 1-bromo-1,3-diphenyl-2-propene. The reaction product precipitated and was recrystallized by the triangle scheme. The high melting isomer **9**, 1.1 g, mp 180.5–182.5° (nmr absorptions centered at *ca.* 5.2), and one lower melting isomer **10**, 0.7 g, mp 137–138° (nmr absorptions of 5.36, 4.56, and 6.12 in deuteriochloroform), were easily obtained. Two other polymorphic forms of the latter, mp 128–129 and 114–115°, were apparent. These showed very similar nmr patterns to the 138° material.

The configurations of **9** and **10** were assigned by means of nmr spectra and by the following reaction. To *erythro*-1,2-dibromo-1,3-diphenylpropane, mp 110°, 5.0 g, was added 2.6 g of N-bromosuccinimide, and the mixture was heated at reflux in

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[37] This can be easily seen if the reader will take the trouble to make the molecular models. The C-1 phenyl of **12** may fairly easily slip past two protons (at C-2 and C-3) to form **13**. However, such rotation is difficult in **11** although it is possible in another C-2,3 conformer of **11**.

[38] S. W. Ela and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 5777 (1966).

carbon tetrachloride for 2 days. The succinimide was filtered off and the remaining solution concentrated. In the absence of equilibration, this bromination could only give EE and ET products as well as 1,1,2-tribromo-1,3-diphenylpropane (**15**). The material **9** was isolated, 9.6 g, mp 181–182°, as well as 0.96 g of **10**, mp 131–133°. A third fraction, mp 93–95°, 1.7 g, was a mixture of starting material and **10**. The remaining oil (1.3 g) was a similar mixture with traces of **15** apparent.

Registry No.—**4**, 16793-35-4; **5**, 16793-36-5; **6**, 16793-37-6; **7**, 16793-38-7; **9**, 16793-39-8; **10**, 16793-40-1.

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The Hydrogenation of Dialkylcyclohexenes with Rhodium Catalysts[1]

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The *cis/trans* product ratios observed in the hydrogenation of six dialkylcyclohexenes on rhodium catalysts at 25° and 1 atm are given. These are compared with the results when platinum and palladium catalysts are used. The effect of temperature on the product ratios from three of these cycloalkenes with rhodium and platinum catalysts are reported, as are the results of their disproportionation and the hydrogenations of the corresponding arenes at 100°. Rhodium and platinum are found to be closely similar, and quite different from palladium, in their promotion of hydrogen addition to carbon unsaturation. Platinum appears to be the more effective of the two for the straightforward addition of hydrogen to 1,2-diadsorbed alkanes.

There have been several reports of the stereochemical results observed when platinum and palladium catalysts are used to effect the hydrogenation of dialkylcycloalkenes which can form *cis* and *trans* products.[2] It seems clearly established that palladium catalysts furnish a product mixture at pressures near one atmosphere which approaches equilibrium composition, whereas platinum catalysts lead to an entirely different mixture. Furthermore, isomerization of the initial cycloalkene has been found to be pronounced with palladium catalysts but to be relatively minor or insignificant for most cycloalkenes with platinum.[2,3] The nonintervention of isomerization with platinum catalysts, even where this is thermodynamically favored, has been demonstrated in recent reports of the kinetics of this reaction[4] and in studies of the competitive hydrogenation of pairs of cycloalkenes.[5]

It was of interest to compare the catalytic properties of rhodium catalysts with those of palladium and platinum. We report here the stereochemical results observed when several dialkylcyclohexenes are hydrogenated over rhodium, together with the effect of temperature on the product ratios using both rhodium and platinum.

Results

The data in Table I summarize the results of the hydrogenations of several dialkylcyclohexenes at 25° near one atmosphere with rhodium, platinum, and palladium catalysts. Most of these data are averages of replicate analyses of replicate hydrogenation experiments (usually three, occasionally more) and include, for rhodium and platinum, the results from several experiments interrupted between 15 and 50% hydrogenation. The data for the hydrogenations using palladium catalysts are all from complete hydrogenations; extensive isomerization of the cycloalkenes are observed with this catalyst and the *cis/trans* product ratios for the unsymmetrical dialkylcyclohexanes vary ±4–5% depending upon the extent of hydrogenation when samples are removed for analysis.[2e] In contrast, isomerization is small at 25° when moderate amounts of rhodium catalysts are used (1–4% near 50% hydrogenation). Isomerization is unobservable with platinum at this temperature. When an excessive amount of rhodium catalyst is used, a hydrogen deficiency is created at the catalyst surface because of transport limitations[6] and isomerization increases. This effect is less pronounced with platinum. However, as long as the amount of catalyst is reasonably small (10–40 mg), the product composition from reactions at 25° is the same, within the ±1% precision of our analyses, at various stages in the hydrogenations with both catalysts. This is not true with palladium.

Table I

Hydrogenation of Dialkylcyclohexenes with Rhodium, Platinum, and Palladium Catalysts[a]

Cyclohexene	% *cis* isomer[b] with— Rh[c]	Pt	Pd
1,4-DiMe	61	57[d]	28[e]
1-Me-4-Et	55	48[d]	24
1-Et-4-Me	55	58[d]	27
1,4-DiEt	54	49	25
1-Me-4-*i*-Pr	52	43[d]	26[e]
1-*i*-Pr-4-Me	54	58[d]	21[e]

[a] In purified glacial acetic acid, 25° (1 atm). [b] Precision of analysis ±1%. [c] 5% on charcoal. [d] Data from ref 2d. [e] Data from ref 2e.

The data in Table II summarize the effect of temperature with three of the cycloalkenes of Table I. At 50° and above, disproportionation to form arenes and cyclohexanes becomes competitive with the hy-

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(1) Support of a part of this research through GP 4656 from the National Science Foundation is gratefully acknowledged.

(2) (a) S. Siegel, *J. Amer. Chem. Soc.*, **75**, 1317 (1953); (b) S. Siegel and M. Dunkel, *Advan. Catal.*, **9**, 15 (1957); (c) S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6082, 6087 (1960); (d) J-F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **82**, 6090 (1960); (e) J-F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **83**, 3874 (1961); (f) S. Siegel and B. Dmuchovsky, *ibid.*, **86**, 2192 (1964).

(3) (a) D. J. Cram, *ibid.*, **74**, 5518 (1952); (b) G. V. Smith and R. L. Burwell, *ibid.*, **84**, 925 (1962); G. C. Bond, J. J. Phillipson, P. B. Wells, and J. M. Winterbottom, *Trans. Faraday Soc.*, **60**, 1847 (1964); (d) G. V. Smith and J. R. Swoap, *J. Org. Chem.*, **31**, 3904 (1966); (e) A. W. Weitkamp, *J. Catal.*, **6**, 431 (1966).

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(6) H. C. Yao and P. H. Emmitt, *J. Amer. Chem. Soc.*, **81**, 4125 (1959).