The Friedel–Crafts Catalyzed Isomerization of the Bromotoluenes

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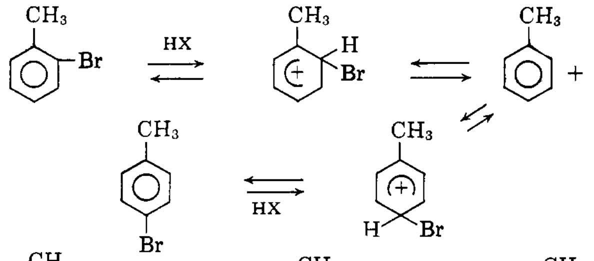
Treatment of *o*-, *m*-, or *p*-bromotoluene with anhydrous aluminum bromide resulted in rapid isomerization to equilibrium at 25°. Disproportionation to toluene and dibromotoluene always accompanied the isomerizations but was negligible when the reaction was carried out in the presence of one or more moles of toluene. The isomeric composition of the reaction mixture as a function of time was determined for isomerization of each bromotoluene isomer in toluene solution, and relative rate constants were calculated for each of the six possible isomeric transformations. The mechanisms of isomerization in the presence and absence of toluene are discussed.

Qualitative observations of the rearrangement of aromatic isomers under the influence of aluminum halides were reported soon after the discovery of the Friedel–Crafts reaction, and a variety of types of aromatic compounds have since been found to isomerize under conditions of the Friedel–Crafts reaction.[2] The literature on isomerization of halogenated aromatics has been reviewed in a series of papers by Olah and co-workers[3] and and in a recent publication by Kooyman.[4] No further summary appears necessary here.

The mechanisms involved in the aluminum chloride-catalyzed isomerization of the monoalkyltoluenes in excess toluene have been discussed in a recent series of papers by Allen and co-workers.[5] It was demonstrated that the mechanism varied from an intramolecular 1,2-shift in the xylene isomerization to an intermolecular alkylation of toluene in the case of *t*-butyltoluene. In each case, it was the more highly branched alkyl group which migrated. For the interconversion of *o*- and *p*-bromotoluene in the absence of solvent, Olah and Meyer[3b] proposed the debromination–bromination scheme shown in equation 1. Their data did not permit differentiation between an analogous intermolecular mechanism and the intramolecular 1,2-shift (equation 2) for formation and isomerization of *m*-bromotoluene.



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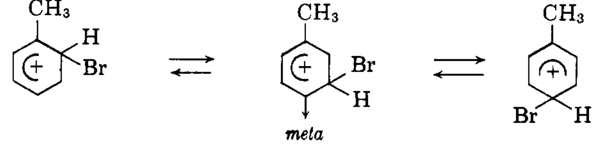

(2)

In the present work, the isomerization of the bromotoluenes was studied without solvent, in the presence of excess toluene and in dilute carbon disulfide solution in an attempt to obtain a clearer understanding of the mechanisms involved and the conditions required for isomerization.

Results

Several common Lewis acids were investigated under a variety of conditions to determine how readily the bromotoluenes would undergo isomerization. Representative runs are collected in Table I.

A number of common Lewis acids did not effect isomerization under the mild conditions (<100°) employed in this study. Thus, *o*-bromotoluene was recovered unchanged after treatment with anhydrous ferric chloride or stannic chloride at 90° or with boron trifluoride etherate or aluminum chloride in nitromethane solution at 25°.

Reaction occurred readily in the presence of aluminum chloride without added co-catalyst, in spite of the very low solubility of aluminum chloride in the medium. Aluminum bromide was a somewhat more effective catalyst, probably due to its ready solubility in the bromotoluene mixture. Addition of hydrochloric acid[6] or water as co-catalyst (runs 49 and 60) resulted in an extremely rapid reaction. In run 60, for example, more than 60% of the *p*-bromotoluene reacted in three minutes at 25° with 0.5% $Al_2Br_6 \cdot H_2O$[7] catalyst. The only catalyst system other than the aluminum halides which was found to be effective was the hydrogen fluoride–boron trifluoride system (run 8) often used in isomerization of alkylbenzenes.[8]

All three bromotoluene isomers isomerized to an equilibrium mixture containing 37% *o*-, 46% *m*-, and 17% *p*-isomer, in agreement with the results of Olah and Meyer.[3b] The position of equilibrium was independent of catalyst, catalyst concentration, or solvent, and was virtually unaffected by temperature[9] over the range −20 to 90°.

No attempt was made to obtain an accurate equilibrium constant for the disproportionation reaction:

$$2BrC_6H_4CH_3 \underset{K_d}{\rightleftarrows} Br_2C_6H_3CH_3 + C_6H_5CH_3$$

The values of K_d calculated from typical "long" runs (such as runs 14 and 15, Table I) were in the range

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[2] *Cf.* C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941.

[3] (a) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *J. Org. Chem.*, **27**, 3441, 3449, 3455 (1962); (b) G. A. Olah and M. W. Meyer, *ibid.*, **27**, 3464 (1962).

[4] E. C. Kooyman and R. Louw, *Rec. trav. chim.*, **81**, 365 (1962).

[5] R. H. Allen, *J. Am. Chem. Soc.*, **82**, 4856 (1960), and earlier papers.

[6] In run 49, the hydrochloric acid served not only as co-catalyst but also to solubilize the aluminum chloride, resulting in a completely homogeneous system.

[7] The expression $Al_2Br_6 \cdot H_2O$ is intended only as a representation of the stoichiometric ratio of Al_2Br_6 and water. The composition of the actual catalytic species is not known.

[8] D. A. McCauley and A. P. Lien, *J. Am. Chem. Soc.*, **74**, 6246 (1952).

[9] The same equilibrium mixture was also obtained from the reaction of 2,4,6-tribromophenol and toluene under the influence of aluminum chloride, conditions which Kohn and Bum[10] reported to yield "essentially pure" *m*-bromotoluene.

[10] M. Kohn and F. Bum, *Monatsh.*, **33**, 923 (1912).

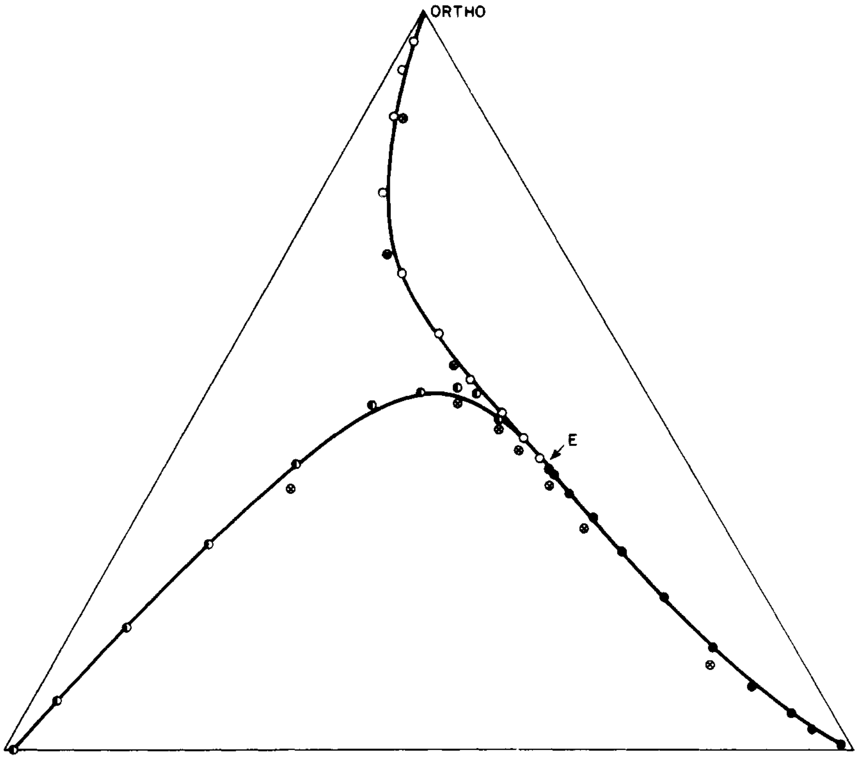

Fig. 1.—Isomerization of bromotoluenes in excess toluene. ◐ = *para*, ● = *meta*, ○ = *ortho*; ⊗ = data of Olah and Meyer (ref. 3b). E = equilibrium point.

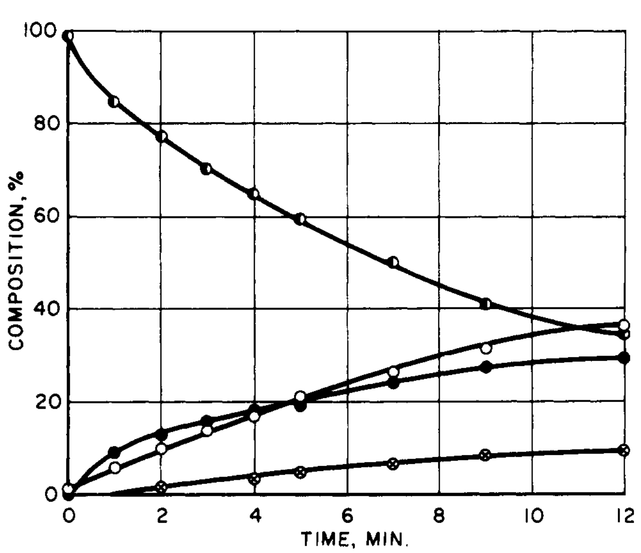

Fig. 2.—Isomerization of neat *p*-bromotoluene with $Al_2Br_6 \cdot H_2O$ catalyst. ◐ = *para*, ● = *meta*, ○ = *ortho*; ⊗ = toluene (mole % based on total bromotoluenes).

0.04–0.06.[11] It is not known whether all of the dibromotoluene isomers were present in equilibrium proportions under these conditions. The analogous disproportionation of bromobenzene has been reported[4,12] to yield $K_d = 0.04$ at 25°.

Addition of an equimolar quantity of water to a concentrated solution of aluminum bromide (Al_2Br_6) in carbon disulfide produced a solution (after filtration) which could be used to catalyze the bromotoluene isomerizations under completely homogeneous conditions. Each bromotoluene isomer in a large excess (10 moles) of toluene was treated with 1 mole % of the $Al_2Br_6 \cdot H_2O$ catalyst at 25° and the isomer compositions followed as a function of time. Under these conditions, disproportionation was negligible (<1%) during the time required to reach equilibrium among the monobromotoluenes. The results of all three runs are plotted on triangular coordinates[13] in Fig. 1. Decreasing the toluene–bromotoluene ratio from 10:1 to 1:1 did not appreciably affect the course of the isomerizations.

To determine the extent of toluene formation during the reaction, the isomerization of *p*-bromotoluene in the absence of toluene was run in the presence of the aluminum bromide–water catalyst. Disproportionation, resulting in the formation of toluene, was slow relative to the isomerization reaction (Fig. 2). This same reaction was then carried out in dilute (*ca.* 0.28 *M*) carbon disulfide solution, with the results shown in Fig. 3. Although the two sets of data (Fig. 2 and 3) appear qualitatively similar, they differ quantitatively in that, for any given concentration of *p*-isomer remaining, the run in carbon disulfide showed: (1) much less toluene formed by disproportionation and (2) a somewhat higher ratio of *o*- to *m*-bromotoluene. The latter effect is quite evident from the trajectories plotted in Fig. 4.

To ascertain whether heterogeneity of the catalyst is an important factor in determining the course of isomerization of *p*-bromotoluene, two runs were made under otherwise identical conditions (equimolar toluene: *p*-bromotoluene, 25°). The catalyst for the homogeneous reaction consisted of less than 1% aluminum chloride (Al_2Cl_6) made soluble with gaseous hydrogen chloride, while 10% solid aluminum chloride served as the heterogeneous catalyst. These two trajectories are also plotted in Fig. 4. Significantly, the homogeneous aluminum chloride–hydrogen chloride system produced a trajectory identical to that obtained with the soluble aluminum bromide catalyst. The solid aluminum chloride run deviated markedly from any of the previous results.

Discussion

It is difficult to compare reaction rates in Friedel–Crafts systems on a quantitative basis. Rates have often been found to be nonreproducible, and the presence of highly basic aromatics, either as impurities or as by-products of the reaction, have led to marked rate depressions.[13] It is clear, however, that the bromotoluenes isomerize orders of magnitude more rapidly than either the chlorotoluenes[3] or bromophenols.[14] Comparison with the alkyltoluenes is more difficult, since the two systems isomerize under approximately com-

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[11] A value of approximately 0.05 has been obtained by A. A. Asadorian (personal communication) for the same equilibrium.

[12] F. Fairbrother and N. Scott, *Chem. Ind.* (London), 998 (1953).

[13] R. H. Allen, T. Alfrey, Jr., and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 42 (1959).

[14] G. Baddeley and J. Plant, *J. Chem. Soc.*, 525 (1943).

Table I

The Aluminum Halide-catalyzed Isomerization of Bromotoluene Isomers at 25°

Run	Reactant[a]	Catalyst (mole %)	Time, hr.	Products[b] *o*	*m*	*p*	Tol.[c]	Br_2 Tol.[c]
1	*o*	Al_2Cl_6 (5)	4	38	41	21	13.6	[d]
8	*o*	HF-BF_3	5[e]	91	5	4	1.1	[d]
13	*o*	Al_2Br_6 (2)	4[f]	71	10	19	1.7	[d]
14	*o*	Al_2Br_6 (3)	65	37.7	45.4	16.9	20.3	20.8
15	*p*	Al_2Br_6 (4.5)	64	36.6	45.5	17.8	25.0[g]	24.1
19	*m*	Al_2Br_6 (2.4)	96	36.5	46.6	16.9	18.1	>15
44	*p*[h]	Al_2Cl_6 (9)	6[e]	45	10	45	[d]	[d]
49	*p*[h]	Al_2Cl_6 + HCl (0.23)	0.5[e]	35	16	49	[d]	[d]
60	*p*	$Al_2Br_6 \cdot H_2O$[i] (0.5)	0.05	35	28	37	8.9	[d]

[a] Starting material: *o*-, *m*-, or *p*-bromotoluene. [b] Expressed as mole % of total monobromotoluenes recovered. [c] Toluene and dibromotoluene formed by disproportionation. [d] Not determined. [e] At 0°. [f] At −20°. [g] Traces of toluene disproportionation products were also formed. [h] Run in the presence of an equimolar amount of toluene. [i] *Cf.* ref. 7.

parable conditions. Comparison of our data with those of Allen, *et al.*, for ethyltoluene[15] and cymene[13] isomerizations shows the probable[16] order of reactivity to be cymene > bromotoluene > ethyltoluene. This does not imply, however, that the relative ease of migration in this system lies in the order *i*-propyl>bromine>ethyl, since the rate-determining steps have not been identified.

The results of Olah and Meyer[3b] for the isomerization of undiluted bromotoluenes are compared directly with the present results in Fig. 1. The two sets of data may be seen to fall nearly within experimental error, in spite of the fact that our reactions were carried out in the presence of excess toluene with a homogeneous catalyst system.[17] This agreement, however, must be considered to be strictly fortuitous, since treatment of undiluted *p*-bromotoluene with the same catalyst system produced an entirely different trajectory (Fig. 4). Furthermore, the use of solid aluminum chloride in the presence of toluene resulted in a further change in the course of the isomerization.[18] In view of these results any extrapolations from homogeneous to heterogeneous systems (or vice versa) would seem ill-advised.

The data in Fig. 1 were treated in the manner described by Allen, *et al.*,[13] for determination of the relative rate constants of the three-component equilibration shown in Scheme 1. The solid lines in Fig. 1 represent the theoretical trajectories calculated from the following set of relative rate constants:

$$\begin{tikzcd} & \textit{ortho} \arrow[dl, shift left, "k_{op}"] \arrow[dr, shift left, "k_{om}"] & \\ \textit{para} \arrow[ur, shift left, "k_{po}"] \arrow[rr, shift left, "k_{pm}"] & & \textit{meta} \arrow[ul, shift left, "k_{mo}"] \arrow[ll, shift left, "k_{mp}"] \end{tikzcd}$$

Scheme 1

$$\begin{aligned} k_{mo} &= 1.0 & k_{mp} &= 1.5 \\ k_{pm} &= 4.2 & k_{po} &= 13.4 \\ k_{op} &= 6.0 & k_{om} &= 1.21 \end{aligned}$$

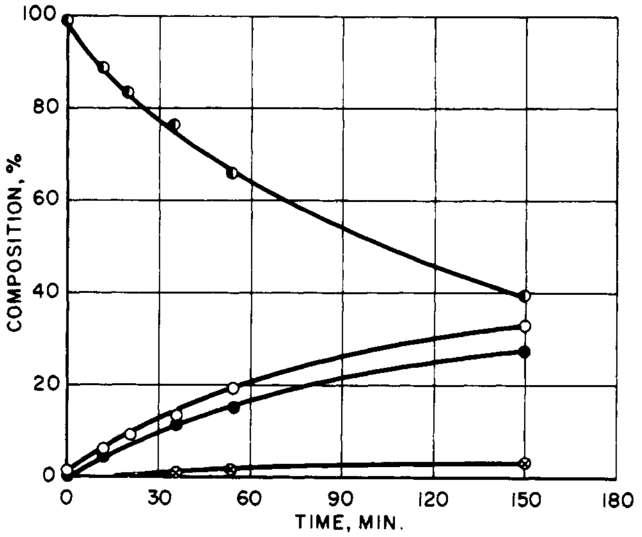
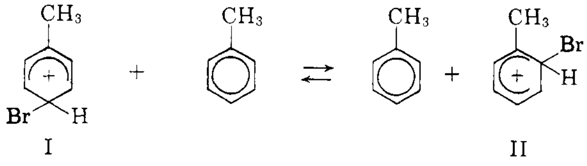


Fig. 3.—Isomerization of *p*-bromotoluene in carbon disulfide with $Al_2Br_6 \cdot H_2O$ catalyst. ◐ = *para*, ● = *meta*, ○ = *ortho;* ⊗ = toluene (mole % based on total bromotoluenes).

The agreement with the experimental values is excellent. The use of a large excess of toluene was intended to maximize the amount of intermolecular isomerization. The relative rate constants are, indeed, consistent with rapid interconversion of the *ortho* and *para* isomers, either *via* the debromination–bromination scheme proposed by Olah[3b] (equation 1) and Kooyman,[4] or by direct bromonium ion transfer from the σ-complex, I or II, to toluene. There is some indication that even under these conditions, *m*-bromotoluene formation occurs predominantly by the intramolecular 1,2-shift (equation 2). Thus, Kooyman[4] states that transbromination experiments with bromobenzene and toluene (equation 4) initially produced *o*- and *p*-bromotoluene



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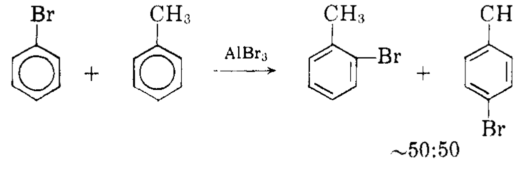

(4)

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[15] R. H. Allen, L. D. Yats, and D. S. Erley, *J. Am. Chem. Soc.*, **82**, 4853 (1960).

[16] Based on the assumption that the initial very rapid isomerization of *p*-cymene is a better measure of its inherent reactivity than the slower reaction which follows.

[17] The "water-promoted aluminum chloride" catalyst used by Olah and Meyer[3b] is not soluble to an appreciable extent in the bromotoluene mixtures

[18] It was actually possible to vary the trajectory at will between the upper two lines of Fig. 4, simply by changing the amount of solid aluminum chloride used as catalyst.

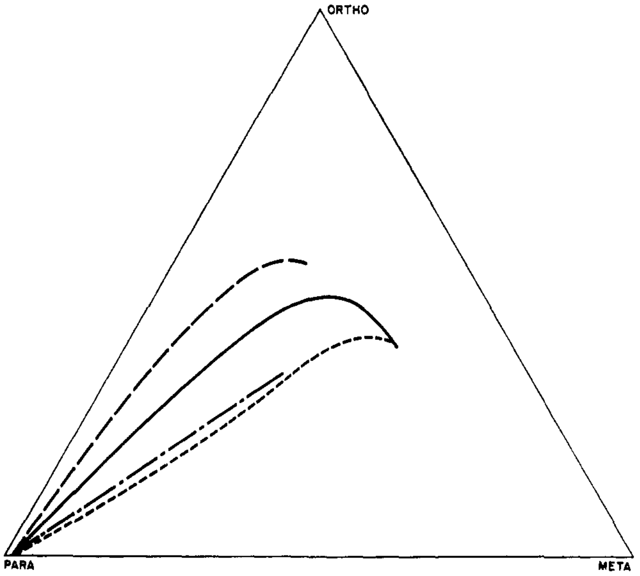
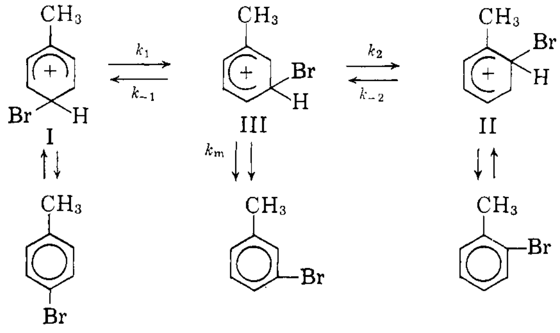


Fig. 4.—Variation in *p*-bromotoluene isomerization trajectory with conditions. ——— = in toluene, $Al_2Br_6 \cdot H_2O$ or $Al_2Cl_6 \cdot HCl$ catalyst; — — — = in toluene, 10% Al_2Cl_6 (solid); - - - - = neat, $Al_2Br_6 \cdot H_2O$ catalyst; — - — = 0.28 *M* in carbon disulfide, $Al_2Br_6 \cdot H_2O$ catalyst.

in comparable proportions. No mention is made of the formation of the *m*-isomer.[19] In contrast, the "transbromination" of toluene with *p*-bromotoluene gave *o*- and *m*-bromotoluene in a ratio of only 3:1 (as measured by the ratio of k_{po} to k_{pm}). This low selectivity might result if the brominating species, *e.g.*, free Br^+, Br_2, or I, were very reactive and consequently nonselective. The substrate selectivity of the brominating species could be estimated from relative rates of isomerization and disproportionation, since disproportionation is the result of the bromination of *p*-bromotoluene, just as isomerization is the result of bromination of toluene. In a reaction employing equimolar quantities of toluene and *p*-bromotoluene, disproportionation occurred to the extent of only 0.2% during the first 30% of isomerization. Isomerization was thus at least 150 times as fast as disproportionation. We would expect any brominating species which discriminates so well between substrates to exhibit high positional selectivity as well.[20] Since the positional selectivity, as measured by k_{op}/k_{om} and k_{po}/k_{pm}, was low, it seems most probable that *m*-bromotoluene formation (and isomerization) occurs principally by an intramolecular 1,2-shift, even in the presence of excess toluene.

Turning now to isomerization of *p*-bromotoluene in the absence of solvent (Fig. 2), a slow, steady build-up of toluene during the reaction was observed without a corresponding increase in the rate of *ortho* isomer formation. This is not consistent with the intermolecular mechanism outlined above for *ortho–para* interconversion in the presence of toluene. Operation of the mechanism outlined in either equation 1 or 3 in the absence of added toluene would require the amount of *o*-bromotoluene to vary as the square of the toluene concentration during the early stages of the reaction. In fact, the two concentrations were very nearly directly proportional in the run shown in Fig. 2. Thus, there must be an independent path for the formation of *o*-bromotoluene which does not involve toluene.[21]

The fact that *m*- and *o*-bromotoluene were formed simultaneously, and at comparable rates, in the reaction plotted in Fig. 2 requires a means of direct *para–ortho* interconversion, without the intermediacy of the *m*-isomer. We propose the series of 1,2-shifts shown in equation 5 to account for the isomerization in the absence of toluene. Direct *para–ortho* interconversion requires only that the 1,2-bromine shift in III occur at a rate comparable to proton loss; *i.e.*, that k_{-1}, k_{-2}, and k_m are of comparable magnitude. Dilution of the reaction mixture with carbon disulfide, as in Fig. 3, apparently decreases the relative rate of the proton transfer, k_m, allowing more of III to undergo 1,2-bromine shift to II. There results a higher *o/m* ratio, without the higher concentration of toluene required by equation 3.



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Experimental

Materials.—*o*-Bromotoluene was prepared in this laboratory by distillation of an *o*–*p*-bromotoluene mixture through a column containing some 200 theoretical plates. Infrared analysis (see below) indicated a composition of 98.8% *o*, 1.2% *p*. A spectroscopic standard was prepared from *o*-toluidine (previously purified through fractional recrystallization of the hydrochloride) by the Sandmeyer procedure.[22] *p*-Bromotoluene was obtained from the same source and was further purified by partial crystallization and redistillation; infrared analysis showed 99% *p*, 1% *m*. *m*-Bromotoluene was obtained from the Eastman Kodak Co. and was fractionally distilled through a 1-ft. Podbielniak column before use. Toluene was fractionally redistilled commercial material. Toluene, bromotoluenes, and carbon disulfide contained less than 0.001 *M* water as determined by Karl Fischer titration. Aluminum chloride (B. and A. resublimed) and aluminum bromide (Amend Drug and Chemical Co.) were used as received unless otherwise noted.

General Isomerization Procedure.—The appropriate bromotoluene isomer and catalyst were transferred to tared glass-stoppered[23] vials and allowed to stand[24] at the desired temperature. Reactions were quenched by addition to water, the organic layer separated and analyzed as described below.

Composition *vs.* Time Curves.—Composition *vs.* time curves were obtained by running the isomerization in a flask equipped

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[19] The results of Kooyman and Louw[4] must be accepted with some caution, however, since they reported that later in the reaction *p*-bromotoluene predominated over the *ortho* isomer, which is not in agreement with the present work. We interpret this to mean that their gas chromatographic method did not distinguish between the *m*- and *p*-isomers. We also have been unable to resolve these isomers by gas chromatography on either packed or capillary columns.

[20] Recent nitration studies by Olah and co-workers [*J. Am. Chem. Soc.*, **83**, 4571 (1961)] have shown that it is possible to have high positional selectivity while obtaining very low substrate selectivity. The reverse, however, has not been demonstrated to our knowledge.

[21] Olah and Meyer[3b] proposed reaction according to equation 1 for their isomerizations of neat bromotoluenes. Without data concerning the amount of disproportionation which occurred in their system, it is impossible to assess the adequacy of their mechanism.

[22] *Cf.* J. L. Hartwell, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 185.

[23] Rubber serum caps were used in some runs with equivalent results.

[24] Those runs which were not homogeneous, *e.g.*, those employing aluminum chloride, were stirred magnetically during reaction.

with a side arm carrying a serum bottle cap. Samples were removed periodically by means of a hypodermic syringe, added immediately to water,[25] and the organic layer analyzed by infrared. A small, positive pressure of nitrogen in the reaction flask prevented contamination of the reaction with atmospheric moisture during sampling.

The reactions plotted in Fig. 1–3 were run with the same prepared catalyst solution in order to avoid any complications arising from differences in the composition of the catalyst. A solution of 4.35 g. (8.1 mmoles) of Al_2Br_6 in 30 ml. of carbon disulfide was treated with 0.140 g. (7.7 mmoles) of water. The mixture was shaken thoroughly and forced with nitrogen through a sintered glass funnel. The clear, yellow catalyst solution was stored in a flask fitted with a serum bottle cap, and aliquots were removed as required with a hypodermic syringe. Isomerizations were carried out in 100-ml. serum bottles. The bromotoluene and solvent, if any, were weighed into the bottle, a serum bottle cap applied and a weighed amount of the above catalyst solution was added from a syringe. Samples were removed by means of a syringe and added to water plus enough carbon disulfide to form a solution of appropriate concentration for infrared analysis. The carbon disulfide layers were separated, dried with anhydrous magnesium sulfate, and analyzed.

Analyses.—The concentrations of the bromotoluene isomers were estimated by quantitative analysis of infrared spectra recorded from carbon disulfide solution on a Perkin-Elmer Infracord spectrometer, Model 137. The out-of-plane hydrogen deformation frequencies at 13.4, 13.0, and 12.5 μ were used for determination of *o*-, *m*-, and *p*-bromotoluene, respectively. Mixtures containing largely a single isomer were run at two concentrations. Alternatively, in mixtures containing only small amounts of the *o*- and *m*-isomers, *p*-bromotoluene was determined at 9.9 μ. When no other materials were present, known mixtures could be determined to ±2% of the amount present. Toluene was similarly estimated from its absorption peak at 13.7 μ. Large amounts of toluene caused interference with the *o*-bromotoluene absorption, and the two were determined by means of simultaneous equations.

o-Bromotoluene could also be estimated by gas chromatography, using a 150 ft. × 0.010 in. capillary column coated with Ucon LB-550-X and operated at 100°. About one third of the samples in the runs shown in Fig. 1–3 were checked in this manner and the agreement with infrared analyses was excellent. Separation of *m*- and *p*-bromotoluene by gas chromatography was not obtained.

Reaction mixtures in which 5% or more disproportionation had occurred could not be analyzed without first removing the dibromotoluenes formed (analysis of the entire mixture gave high values for the *p*-isomer). This was accomplished either by fractional distillation or by preparative scale v.p.c. (5 ft. × 1/2 in. column packed with Ucon LB-550-X on Chromosorb P). When distillation was used, each fraction was analyzed by infrared and the fractions analyzed contained at least 96% of the monobromotoluenes present before distillation. The preparative v.p.c. method was used also to check a number of reaction mixtures which had been analyzed directly by infrared. The agreement obtained (Table II) indicated that there was no serious interference in the total reaction mixture.

Table II

Comparison of Direct Analysis of Reaction Mixtures and Analysis After Preparative V.p.c.

	o	*m*	*p*
Before v.p.c.	37.7	45.9	16.4
After v.p.c.	38.0	45.0	17.0

Table III

Comparison of V.p.c. and Infrared Analyses of Bromotoluene Isomerization Mixtures

V.p.c. (wt. %)			Infrared (wt. %)	
Toluene	Bromotoluene	Dibromotoluene	Toluene	Bromotoluene[a]
1.2	98.3	...	1.0	99.0
25.9	74.1	...	25.3	74.7
...	65.4	34.6	...	61.5
6.9	72.9	20.2	6.6	71.8

[a] Sum of analyses for the three individual isomers.

Dibromotoluene was determined by v.p.c. (10 ft. × 1/4 in. column, Dow Corning silicone oil 550 on Celite, 170°), relating peak area to mole % by means of correction factors determined from known mixtures.[26] At the same time, toluene and bromotoluene could be readily determined and the values compared with those obtained by infrared. The agreement (Table III) served as a further check on the reliability of the infrared analyses.

Acknowledgment.—The authors are indebted to Professor J. C. Martin of the University of Illinois and Professor H. M. Walborsky of Florida State University for very stimulating discussions of the mechanism and to Mr. F. L. Beman and Dr. G. A. Olah for making the results of their investigations available prior to publication.

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[25] Equivalent results could be obtained from the aluminum cloride-catalyzed reactions by adding the reaction mixture directly to carbon disulfide, filtering, and recording the infrared spectrum of the filtrate.

[26] A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31** (2), 230 (1959).

The *cis–trans* Isomerization of Some Simple Ethylene Derivatives

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The position of the *cis–trans* equilibrium has been determined for four simple chlorinated propenes (III–VI) and two substituted acrylonitriles. Equilibrium was approached from each isomer by the familiar bromine-catalyzed isomerization. The amount of *cis* isomer present at equilibrium is discussed in terms of favorable dipole–dipole interactions between dissimilar substituents.

Although considerable information is available concerning the relative stabilities of the *cis* and *trans* forms of the dihaloethylenes[2,3] and of a number of olefins,[4] very little is known about isomerization of halogenated propenes, butenes, etc., in which the double bond carries both alkyl and halogen substituents. Harwell and Hatch[5] found that the equilibrium mixture of 1-bromopropenes contained 68% of the *cis* and 32% of the *trans* isomer at 0–100°. Predominance of the *cis* form at equilibrium has also been reported qualitatively for 1-iodopropene[2] and 1-chloropropene.[6]

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[2] H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).

[3] (a) A. R. Olson and W. Maroney, *J. Am. Chem. Soc.*, **56**, 1322 (1934); (b) R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 3259 (1939).

[4] For leading references see M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 340–344.

[5] K. E. Harwell and L. F. Hatch, *J. Am. Chem. Soc.*, **77**, 1682 (1955).

[6] M. Craen dissertation, Univ. Brüssel, 1924, p. 45; quoted by Viehe ref. 2.