

product had properties, b.p. 103° (15 mm.) and  $n_D^{27}$  1.5120, which agreed favorably with those in the literature.<sup>18</sup>

One gram of the material prepared by reduction of the unsaturated acetal was subjected to hydrolysis by procedures subsequently described in the study of the hydrolysis of phenylvinylcarbinyl acetal. Using the techniques of separation of 1-phenyl- and 3-phenyl-1-propanols as their *p*-nitrobenzoate esters, 0.4 g. of 1-phenyl-1-propyl *p*-nitrobenzoate and none of the isomeric ester was isolated from the hydrolysate.

**Hydrolysis of Phenylvinylcarbinyl Acetal.**—A 1.088-g. sample of this acetal was dissolved in 75 ml. of 0.304 *N* sulfuric acid in 78% aqueous dioxane. Dry nitrogen gas was bubbled through the solution (which was held at 25°) to sweep out acetaldehyde as it formed in order to minimize chances of back reaction. Five-ml. aliquots of the reaction mixture were removed periodically and were quenched in 25 ml. of 5% aqueous sodium carbonate. The carbinol was extracted from these solutions with ether. The dried ether extracts were subjected to hydrogenation over 0.01 g. of platinum oxide at a pressure of 25 lb./sq. in. for 45 minutes. The ether was then removed *in vacuo*, and the residue was treated with 0.3 g. of *p*-nitrobenzoyl chloride in 5 ml. of anhydrous pyridine. After 24 hours this mixture was extracted with four 50-ml. portions of ether. These combined extracts were washed with 10% aqueous sodium carbonate, dried and evaporated under reduced pressure. The residue was dissolved in a total of 8 ml. of Skellysolve B. The solution was applied to a chromatographic column packed with the fluorescent mixture described by White and Dryden,<sup>19</sup> which consisted of silicic acid-diatomaceous filter aid (2-1) impregnated with rhodamine 6 G. The column was developed with a 5% solution of ether in Skellysolve B. Under fluorescent light separation of two dark bands was observed almost immediately. These were collected separately by elution into weighed containers. After these samples were evaporated, the residual yellow oils were re-

frigerated to produce crystallization. In some cases a single seed crystal of the appropriate ester was added. Crystals from the lower band melted from 55–57° and gave no depression when mixed with authentic samples of 1-phenyl-1-propyl *p*-nitrobenzoate.<sup>20</sup> The products from the upper band melted from 45.5–47° and gave no depression with 3-phenyl-1-propyl *p*-nitrobenzoate.<sup>20</sup> In theory analysis of a 5-ml. aliquot on completion of hydrolysis should have provided a total of  $4.95 \times 10^{-4}$  mole of mixed *p*-nitrobenzoates. From the aliquot taken at 780 min. (Table I) a total of  $4.82 \times 10^{-4}$  mole of *p*-nitrobenzoates was recovered. Chromatographic separation of known mixtures of varying composition of the two *p*-nitrobenzoates was always accomplished with better than 99% over-all recovery.

Authentic samples of 3-phenyl-1-propanol required for these experiments were prepared in 91% yield by reduction of cinnamyl alcohol by the procedures used in the reduction of phenylvinylcarbinol. The properties of the product, b.p. 103–5° (6 mm.),  $n_D^{20}$  1.5349, were in agreement with those reported previously.<sup>21</sup>

**The Response of Phenylvinylcarbinol to Procedures Used in Following the Hydrolysis of its Acetal.**—A solution of 1.344 g. of phenylvinylcarbinol in 75 ml. of 0.304 *N* sulfuric acid in 78% aqueous dioxane was maintained at 25°. Five-ml. aliquots of this solution were removed periodically and were subjected to reduction, esterification and chromatographic procedures as applied in the study of the hydrolysis of phenylvinylcarbinyl acetal. The results of these analyses on samples taken at various times are summarized in Table II.

**Acknowledgment.**—The authors are indebted to Professor E. P. Painter for many helpful suggestions concerning this research and to Professor R. E. Kepner and Mr. Robert Ikeda for help with the chromatographic separations.

(20) L. F. King, *THIS JOURNAL*, **61**, 2386 (1939).

(21) (a) J. B. Conant and W. R. Kirner, *ibid.*, **46**, 242 (1924); (b) J. W. Brühl, *Ann.*, **200**, 191 (1879).

DAVIS, CALIFORNIA

(18) (a) R. C. Huston and T. E. Friedmann, *THIS JOURNAL*, **40**, 785 (1918); (b) J. F. Norris and F. Cortese, *ibid.*, **49**, 2645 (1927).

(19) J. W. White, Jr., and E. C. Dryden, *Anal. Chem.*, **20**, 853 (1948).

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY, HARVARD UNIVERSITY]

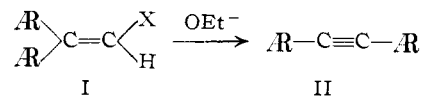
## Stereochemistry of the Rearrangement Involving Migration between Multiply-bonded Carbons

BY AKSEL A. BOTHNER-BY

RECEIVED DECEMBER 22, 1954

*cis*- and *trans*-1-*p*-bromophenyl-1-phenyl-2-bromoethylene-1-<sup>14</sup>C have been prepared and converted by means of potassium *t*-butoxide in *t*-butyl alcohol to labeled 4-bromotolans. The measured radioactivities of the benzoic and *p*-bromobenzoic acids obtained by oxidation of the tolans indicated that the *cis* (bromine and *p*-bromophenyl *cis*) isomer rearranged with 88% migration of the phenyl group while the *trans* isomer rearranged with 92% migration of the *p*-bromophenyl group. Possible mechanisms and implications are discussed.

**Introduction.**—More than sixty years ago it was demonstrated by Fritsch,<sup>1</sup> Buttenberg<sup>2</sup> and Wiechell<sup>3</sup> that the treatment of 1,1-diaryl-2-haloethylenes (I) with sodium ethoxide at 180–200° resulted in a reaction involving elimination and rearrangement to yield substituted tolans (II). Apparently related rearrangements were reported by Tiffeneau<sup>4</sup> (the conversion of 1-bromo-2-phenylpropene to 1-phenylpropyne with molten potassium hydroxide) and more recently by Newman and Kutner<sup>5</sup> (the formation of tolan from 5,5-diphenyl-3-nitroso-2-oxazolidones by alkaline hydrolysis). Potassium amide in liquid ammonia is a particularly suitable



reagent for bringing about the Fritsch–Buttenberg–Wiechell (FBW) rearrangement according to Coleman, *et al.*,<sup>6</sup> who were able by its use to obtain consistently high yields in short reaction times. The rearrangement presents several unusual features, in particular the migration of an aryl group between multiply-bonded carbons.

A striking parallel exists between this rearrangement and the Beckmann rearrangement which is now generally believed to occur by migration of a group between multiply-bonded carbon and nitro-

(1) P. Fritsch, *Ann.*, **279**, 319 (1894).

(2) W. P. Buttenberg, *ibid.*, **279**, 327 (1894).

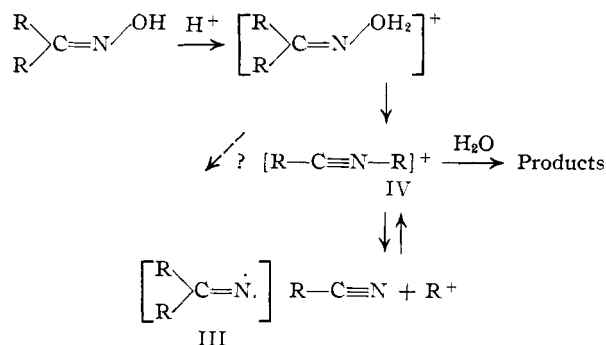
(3) H. Wiechell, *ibid.*, **279**, 337 (1894).

(4) M. M. Tiffeneau, *Compt. rend.*, **135**, 1374 (1902).

(5) M. S. Newman and A. Kutner, *THIS JOURNAL*, **73**, 4199 (1951).

(6) G. H. Coleman and R. D. Maxwell, *ibid.*, **56**, 132 (1934); G. H. Coleman, W. H. Holst and R. D. Maxwell, *ibid.*, **58**, 2310 (1936).

gen.<sup>7</sup> The formation of an intermediate (IV) in which the carbon-nitrogen bond approaches a triple bond in character is a reasonable hypothesis. The occurrence of a reversible reaction leading to nitrile and carbonium ion (or equivalent) accounts on the one hand for the products obtained in the second-order Beckmann rearrangement, and on the other for the common nature of the products obtained from the Beckmann rearrangement and the reaction of olefins and nitriles in strong acid.<sup>8</sup> The linear arrangement of such an intermediate is also



consistent with crystallographic data on such isoelectronic compounds as acetonitrile-boron trifluoride complex.<sup>9</sup> There are, of course, fundamental differences in the two reactions; for instance the FBW rearrangement is initiated by strong base, while the Beckmann is initiated only by acids. In the light of these considerations, and in view of the well-demonstrated nature of the stereospecificity in the Beckmann rearrangement,<sup>7</sup> it was felt of interest to ascertain whether a similar stereospecificity exists in the FBW rearrangement.

The rearrangement of a compound such as *cis*- or *trans*-1-*p*-bromophenyl-1-phenyl-2-bromoethylene (VI or VII) will yield the same 4-bromotolan regardless of which group migrates. In order to establish the direction of migration the two geomet-

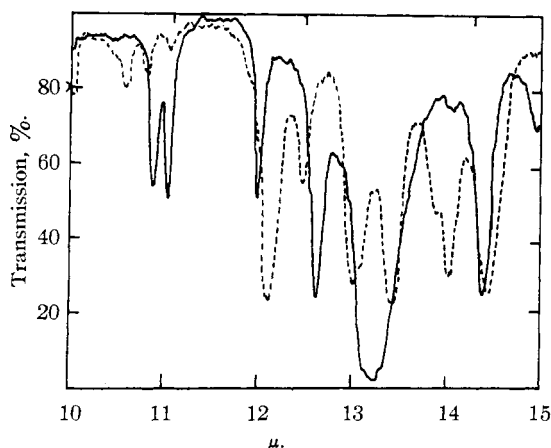


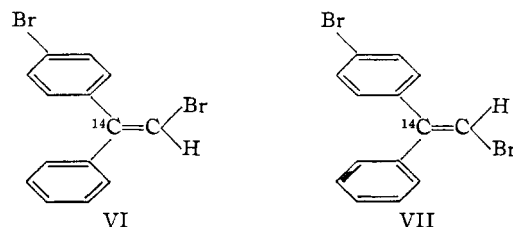
Fig. 1.—Infrared absorption spectra of the isomeric 1-*p*-bromophenyl-1-phenyl-2-bromoethylenes: — isomer melting at 43.0–44.0°; --- isomer melting at 106.0–106.4°.

(7) E. g., G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 440 ff., 483.

(8) J. J. Ritter and P. P. Minieri, *THIS JOURNAL*, **70**, 4045 (1948); H. Wieland and E. Doerrer, *Ber.*, **64**, 2516 (1931).

(9) S. Geller and O. N. Salmon, *Acta Cryst.*, **4**, 279 (1951).

rical isomers of this compound have been prepared with an isotopic label (<sup>14</sup>C) in the 1-position of the two-carbon chain. If the rearrangement of one of these isomers proceeds with exclusive migration of the phenyl group, the resulting 4-bromotolan on oxidation will clearly yield *p*-bromobenzoic acid containing all of the original activity and non-radioactive benzoic acid. Exclusive migration of the *p*-bromophenyl group, or a mixed reaction, also will give easily interpretable results.



In order to distinguish clearly between steric control of the migration ratios and control exercised by the nature of the migrating groups it is necessary to perform the rearrangement on both geometrical isomers (VI and VII). The labeled compounds were prepared following the synthesis of Stoermer and Simon,<sup>10</sup> who reported that the two isomers melt at 43 and 107°. Trial experiments showed that the 107° isomer easily could be obtained pure by fractional crystallization, that a fairly satisfactory separation of the 43° isomer could be achieved by a combination of elution chromatography and fractional crystallization and that the two isomers showed sufficiently different infrared absorption spectra in the 10–15 μ range (Fig. 1) so that the spectra could be used to detect small amounts of one isomer contaminating the other. The purest specimens obtained, from which the spectra of Fig. 1 were taken, melted at 43.0–44.0° and 106.0–106.4° (uncor.).

Complete removal of radioactive 107° isomer from radioactive 43° isomer for the tracer experiments was accomplished by the device of recrystallizing portions of pure inactive 107° isomer from the mother liquor containing the 43° isomer until essentially inactive high-melting isomer was recovered. The active low-melting isomer then could be crystallized out contaminated with a small percentage of inactive high-melting isomer which did not interfere in the tracer experiment.

Rearrangement with potassium amide in liquid ammonia was complicated by reaction with the nuclear halogen giving mainly acid-soluble products. However prolonged refluxing of a solution of either isomer in *t*-butyl alcohol with one and one-half equivalents of potassium *t*-butoxide resulted in a smooth conversion to 4-bromotolan, m.p. 83–85°. Oxidation of the tolan with sulfuric acid-potassium dichromate mixture yielded a mixture of benzoic and *p*-bromobenzoic acids which was separated by a combination of fractional sublimation and crystallization from water. Samples of the unrearranged material, the tolan, and the two acids were then converted to carbon dioxide, and the activities determined by gas-phase proportional counting.

(10) R. Stoermer and M. Simon, *Ann.*, **342**, 1 (1905).

### Experimental

**Sodium Acetate- $1^{14}\text{C}$ .**—Sodium acetate- $1^{14}\text{C}$  was obtained from the Nuclear Instrument and Chemical Co., Chicago, Ill., on authorization from the U. S. Atomic Energy Commission.

**Acetyl Chloride- $1^{14}\text{C}$ .**—The procedure of Strecker<sup>11</sup> was employed. Freshly fused sodium acetate containing 0.1 mc. of  $^{14}\text{C}$  was treated with 7.00 ml. of freshly distilled benzoyl chloride in a 25-ml. distilling flask fitted with a receiver in the form of a side-arm test-tube bearing a drying tube charged with potassium hydroxide pellets, and cooled to  $-30^\circ$ . Gentle application of heat initiated a rather vigorous exothermic reaction, the heat of which was sufficient to distill about a milliliter of liquid into the receiver. When the reaction had subsided, heat was applied externally until the vapor temperature reached  $100^\circ$ . The flask was allowed to cool, then 3 ml. of carrier acetyl chloride was added to the pot, mixed with the contents, and distilled into the receiver as before. The total crude yield was 2.95 g., which was used directly for the acylation of bromobenzene.

***p*-Bromoacetophenone-(carbonyl)- $1^{14}\text{C}$ .**—The procedure followed was that of Adams and Noller,<sup>12</sup> substituting acetyl chloride for acetic anhydride. Starting with 2.95 g. of acetyl chloride- $1^{14}\text{C}$ , a yield of 3.49 g. (47%) of *p*-bromoacetophenone-(carbonyl)- $1^{14}\text{C}$  was obtained. It was isolated by crystallization from low-boiling petroleum ether, rather than distillation, and formed colorless plates, m.p.  $52\text{--}53^\circ$ .

**1-*p*-Bromophenyl-1-phenylethylene- $1^{14}\text{C}$ .**—A solution of *p*-bromoacetophenone-(carbonyl)- $1^{14}\text{C}$  (3.49 g.) in 20 ml. of ether was added dropwise to a solution of Grignard reagent prepared from 5.5 g. of bromobenzene, 1.0 g. of magnesium turnings and 40 ml. of ether. The reaction mixture was refluxed overnight, then hydrolyzed by slow addition of 10% sulfuric acid. After a further 4-hour period of reflux the clear layers were separated, and the water layer extracted with an additional 20 ml. of ether. The combined extracts were dried with sodium sulfate, and the ether was evaporated on a steam-bath. The residual oil weighed 4.65 g., or near theoretical for the reaction. The oil was used directly in the next step.

**1-*p*-Bromophenyl-1-phenyl-2-bromoethylene- $1^{14}\text{C}$  (107° Isomer).**—To a solution of the oil obtained in the last step in 20 ml. of carbon disulfide was added dropwise with stirring a solution of bromine (0.93 ml.) in 10 ml. of carbon disulfide. The bromine was absorbed as fast as it was added, and hydrogen bromide was evolved. The carbon disulfide was distilled off on a steam-bath, 10 ml. of ligroin (b.p.  $60\text{--}90^\circ$ ) was added, and the solution set aside overnight. The mother liquor was then decanted from the large crystals of high-melting isomer which had appeared, and an additional 0.5 g. of inactive high-melting isomer was added as a carrier. Crystallization was allowed to proceed for one week, and the second crop of 107° isomer was then collected. The crops were combined and recrystallized twice from ligroin, yielding 1.10 g. (18%) of colorless crystals in the form of small truncated pyramids with sharply defined facets, m.p.  $106.0\text{--}106.4^\circ$ .

**43° Isomer.**—The mother liquors from the second crop of crystals of high-melting isomer were diluted to 50 ml. with low-boiling petroleum ether and passed through a column of alumina  $1 \times 10$  cm. (Merck Aluminum Oxide, "suitable for chromatographic adsorption") eluting with ten 50-ml. portions of freshly distilled petroleum ether. Colored impurities were retained on the column, and slow evaporation of the fractions resulted in the formation of crystalline material in the first three. The oily portions of all the fractions were combined and dissolved in 10 ml. of ligroin (b.p.  $60\text{--}90^\circ$ ). From this solution six successive 0.4-g. portions of pure inactive 107° isomer were recrystallized. The last crop of high-melting material after two further crystallizations showed no detectable radioactivity. The ligroin then was removed by distillation, the residual oil taken up in 4 ml. of low-boiling petroleum ether and allowed to remain in the cold room overnight. A small seed crystal of low-melting isomer was added, and after two weeks there had crystallized out 0.26 g. (4%) of colorless flat needles, contaminated with a few of the characteristic crystals of the high-melting isomer, which were removed by hand-picking

(11) H. J. Strecker, in M. Calvin, *et al.*, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 176.

(12) R. Adams and C. R. Noller, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 109.

as much as possible. A small sample of the needles melted at  $42\text{--}44^\circ$ .

**4-Bromotolan- $x^{14}\text{C}$ .**—A solution of 0.95 g. of 1-*p*-bromophenyl-1-phenyl-2-bromoethylene- $1^{14}\text{C}$  in 5 ml. of *t*-butyl alcohol in which had been dissolved 150 mg. of potassium metal was refluxed for three days. A mixture of 20 ml. of water and 10 ml. of *t*-butyl alcohol was added, and a homogeneous solution resulted on warming. On cooling, 0.71 g. (near quantitative) of slightly yellowish flat plates crystallized. Washing with cold methanol gave material melting at  $80\text{--}82^\circ$ , raised to  $83\text{--}85^\circ$  by recrystallization from ligroin (b.p.  $60\text{--}90^\circ$ ).

Similar results were obtained with low-melting isomer, which had been diluted with inactive material to simplify the manipulations.

Trial runs with inactive material yielded an analytical sample, colorless plates, m.p.  $83\text{--}85^\circ$ .

*Anal.*<sup>13</sup> Calcd. for  $\text{C}_{14}\text{H}_9\text{Br}$ : C, 65.39; H, 3.53. Found: C, 65.32; H, 3.68.

**Oxidation to Benzoic and *p*-Bromobenzoic Acids.**—A mixture of 0.45 g. of 4-bromotolan- $x^{14}\text{C}$ , 1.00 g. of powdered potassium dichromate and 3.0 ml. of 3.4 *M* sulfuric acid was refluxed for one-half hour, then cooled, diluted with water and extracted with ether (two 5-ml. portions). The ether was shaken with saturated aqueous bicarbonate solution, and the extract was acidified yielding a greenish precipitate of mixed acids. An additional passage through the ether-bicarbonate cycle gave colorless material which was dried, then placed in a sublimator, and subjected to sublimation at 15 mm. pressure at  $60^\circ$ . The first fraction which sublimed was dissolved in hot water (5 ml.). The solution was allowed to cool and all insoluble matter removed. Benzoic acid then was recovered by ether extraction and purified by sublimation; yield 11 mg., m.p.  $120\text{--}121^\circ$ . The pot residue in the sublimator was recrystallized from aqueous ethanol, and purified by sublimation under 1 mm. pressure at  $100^\circ$ . The yield was 0.12 g., m.p.  $251\text{--}252^\circ$ .

Oxidation with neutral permanganate in aqueous dioxane was not as satisfactory.

**Radioassays.**—In the case of the series of products from the high-melting isomer, two experiments were performed, using the same starting material. In experiment A, the analyses were performed at Brookhaven National Laboratory by a method involving dry combustion to carbon dioxide,<sup>14</sup> and proportional counting in the gas phase, using a tube filling of carbon dioxide, argon and methane. In experiment B, and in the experiment with low-melting isomer, the procedure involved wet combustion to carbon dioxide, and proportional counting using a filling of carbon dioxide and methane. When the results were normalized using a factor obtained from the radioassay of a standard sample of active benzoic acid, the radioassays for the samples from experiment A and experiment B were concordant within experimental error.

### Results

The specific radioactivities of the various samples expressed in units of microcuries per millimole are listed in Table I. Examination of the figures reveals that (1) the radioactivity material balance is satisfactory, and (2) the results are quite reproducible. It is also apparent that the reaction is not entirely stereospecific, although phenyl migration

TABLE I

Compound	Specific activities		
	High melting isomer Expt. A	Low melting isomer Expt. B	Low melting isomer
1- <i>p</i> -Bromophenyl-1-phenyl-2-bromoethylene- $1^{14}\text{C}$	1.17	1.16	0.51
4-Bromotolan- $x^{14}\text{C}$	1.14	1.15	.50
Benzoic acid-(carboxyl)- $1^{14}\text{C}$	0.13	0.13	.46
<i>p</i> -Bromobenzoic acid-(carboxyl)- $1^{14}\text{C}$	0.98	0.97	.04

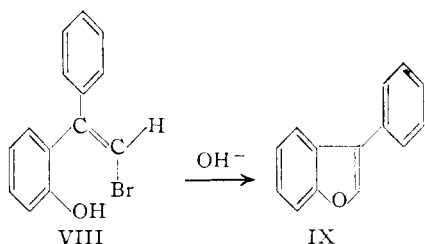
(13) Microanalysis by the microanalytical laboratory, Massachusetts Institute of Technology.

(14) R. C. Anderson, Y. Delabarre and A. A. Bothner-By, *Anal. Chem.*, **24**, 1298 (1952).

occurs more frequently than *p*-bromophenyl migration by a factor of 7.5:1 in the rearrangement of the 107° isomer, while the *p*-bromophenyl migration predominates by 11.5:1 in the 43° isomer.

### Discussion

In order to discuss possible mechanisms for the reaction it is necessary to assign the proper geometric configurations to the two isomers. Stoermer and Simon,<sup>14</sup> who first prepared the two isomers, assigned the *cis* configuration (bromine and *p*-bromophenyl *cis*) to the lower melting isomer, but their assignment rests on two assumptions of dubious validity: (1) that the one isomer of 1-phenyl-1-*o*-hydroxyphenyl-2-bromoethylene which reacts with alkali to yield 2-phenylbenzofuran (IX), necessarily has the *cis* configuration (VIII), and (2), that since this isomer was the lower melting, the *trans* configuration could be assigned to all the higher

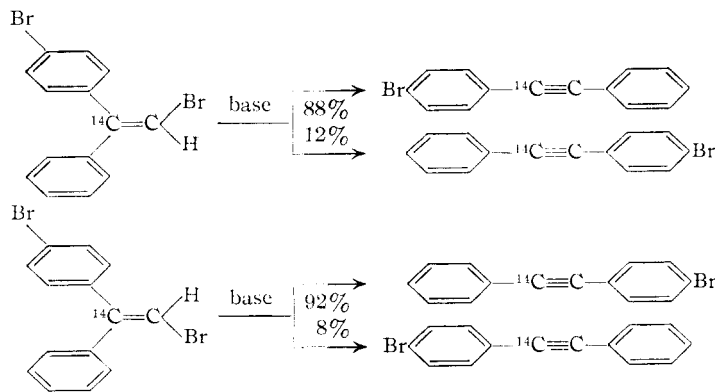


melting isomers of 1,1-diaryl-2-haloethylenes with a substituent in one of the aromatic rings.

The reverse assignment (high melting isomer-*cis*) was made by Bergmann, *et al.*,<sup>15</sup> on the basis of dipole moment measurements on the 1-phenyl-1-*p*-bromophenyl-2-bromoethylenes, and the 1-phenyl-1-*p*-chlorophenyl-2-bromoethylenes. This is in accord with the somewhat analogous case of 1-*p*-chlorophenyl-1,2-diphenyl-2-bromoethylenes.<sup>16</sup>

The dipole moment reported by Bergmann for *trans*-1-*p*-bromophenyl-1-phenyl-2-bromoethylene (1.22D) is larger than seems reasonable, but it is very unlikely that the measurements are in error sufficiently to reverse the configurational assignments.

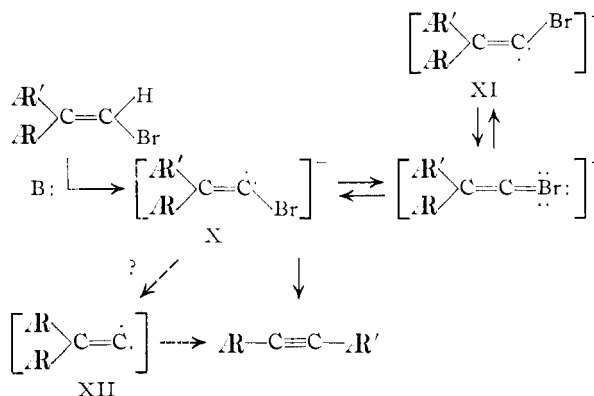
On the assumption that the assignment according to Bergmann is correct the course of the reaction may be written



(15) E. Bergmann, L. Engel and H. Meyer, *Ber.*, **65B**, 446 (1932).

(16) (a) E. Bergmann, *J. Chem. Soc.*, 402 (1936); (b) D. Y. Curtin and E. E. Harris, *This Journal*, **73**, 2716 (1951).

In view of the variety of strong bases which can initiate the rearrangement, a plausible first step in the reaction is the abstraction of a proton with the formation of the anion X. It is suggested that the rearrangement then occurs from the anion in a concerted step involving migration of the aryl group *trans* to the leaving halogen. Implicit in the suggestion is the allotment of some degree of configurational stability to the anion (X).<sup>17</sup> The occasional migration of the group originally *cis* to the



leaving halogen is explained by the competing isomerization of the anion (X), possibly *via* an intermediate with a linear C-C-Br arrangement, made possible by valence shell expansion of the bromine, alternatively by simple thermal isomerization. The degree of stereospecificity in any given case will then be a function of the relative rates of rearrangement and isomerization of the anions (X and XI).

An alternative reaction path involving elimination to give an intermediate with an open sextet (analogous to the intermediate III sometimes suggested for the Beckmann rearrangement) is conceivable, but requires that the intermediate be able to preserve its asymmetry by virtue of the electron distribution alone. Such a hypothesis does violence to the tenets of quantum mechanics, and may be rejected. Preservation of the asymmetry by alteration of the original bond angles is simply an alternative way of describing participation by the migrating group, and is a consequence of the first mechanism described above.

**Acknowledgments.**—I am very grateful to Dr. D. Christman for the radioassays in experiment A, as well as for much helpful correspondence on radioassay methods, and to the Research Corporation for a grant covering the cost of radioassay equipment.

CAMBRIDGE, MASS.

(17) There is of course abundant analogy for such a supposition, *e.g.*, stability of the isoelectronic oximes, the retention of configuration in the methanolysis and carbonation of vinylolithium reagents (ref. 15b and *ibid.*, **73**, 4519 (1951)), and the production of *cis*-stilbenes on decarboxylation of certain *trans*-phenylcinnamic acids (further ref. in ref. 16b).