metry. Apparently, the physical properties of the β-form approximate those of the cyclic monomer. Correspondingly the polymorphic change is associated with an increase in C–H and a decrease in C–O (ether) bond forces (see Fig. 1). This can be attributed to the flexibility of the helical structure of the polymeric chain which is able to assume two or more modes of packing.

Mechanism of Reversible Polarization.—Figure 2 represents a schematic projection of spiral arrangement for the polymeric chain[21] and intends to illustrate the steric course of the reversible polymerization reaction. As a matter of fact it depicts an intramolecular ester interchange process[5] occuring in a concerted fashion bound to produce cyclic monomers. This picture is consistent with our infrared and X-ray data showing that heat treatment results in the weakening of the C–O (ether) bond forces and in shortening of spacing in the polymeric chain. A reversal of such a process can furnish an illustration for the formation of poly-esters from six-membered cyclic esters. Conceivably an axial ethyl group positioned at carbon atom 2 of the diol moiety (Ie and Ib) is bulky enough to exert hindrance to such an arrangement as proposed above. The axial methyl group, however, is able to exert only diminishing effect upon the tendency of cyclic monomers to undergo reversible polymerization.

It is clear that the proposed helical structure for the polymeric chain of neopentylene carbonate provides for the moment a reasonable assumption for the data presented above. Similarly, the idea that axial ethyls at carbon atom 2 of the diol moiety have a determining effect on the prevention of polymerization is supported by the data produced, but still it should be regarded as tentative until more data are obtained.

Acknowledgment.—The X-ray analysis was performed at the Department of Physics, The Hebrew University. The authors are indebted to Dr. Benjamin Fraenkel and Mr. Zvi Kalman of that Department for assistance. We are also indebted to Eastman Kodak Co. for a gift of neopentyl glycol.

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[21] This formula is a stylized representation of the assumed conformation of the helix. It is not intended to be an accurate perspective or orthogonal projection.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

Reaction of Stereoisomeric C^{14}-Labeled 1-Bromo-2,2-diarylethylenes and β-Bromostyrenes with Butyllithium[1]

BY DAVID Y. CURTIN, EDMUND W. FLYNN[2] AND ROBERT F. NYSTROM

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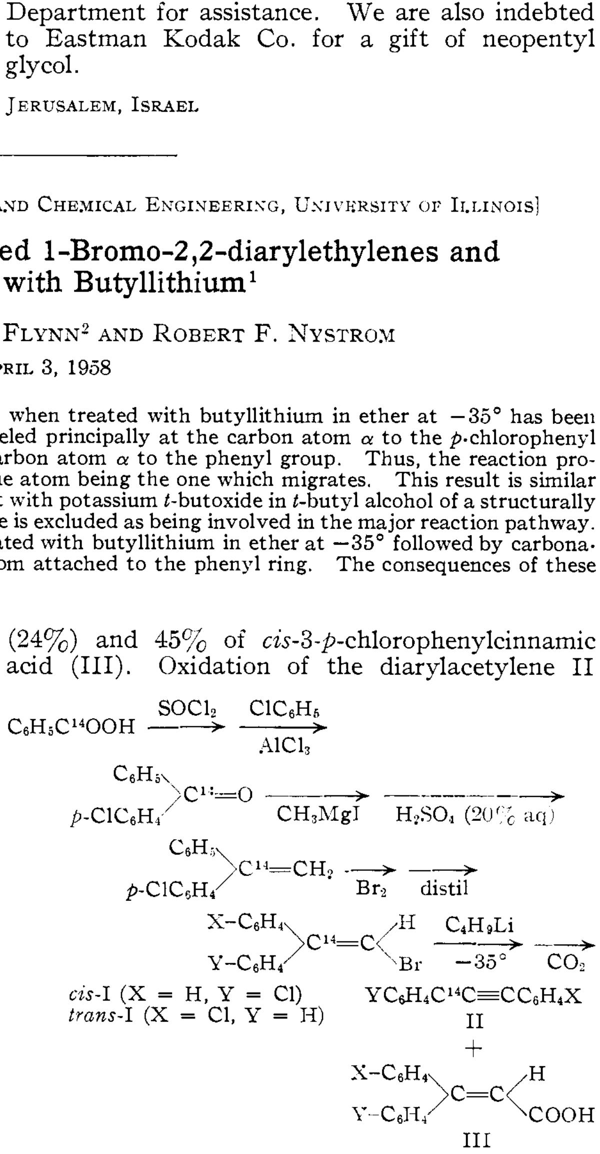
cis-1-Phenyl-1-*p*-chlorophenyl-2-bromoethylene-1-C^{14} (*cis*-I), when treated with butyllithium in ether at −35° has been shown to rearrange to give *p*-chlorodiphenylacetylene (II) labeled principally at the carbon atom α to the *p*-chlorophenyl group: Similarly, *trans*-I gives II labeled principally at the carbon atom α to the phenyl group. Thus, the reaction proceeds stereospecifically with the aryl group *trans* to the bromine atom being the one which migrates. This result is similar to that reported by Bothner-By in a study of the rearrangement with potassium *t*-butoxide in *t*-butyl alcohol of a structurally similar pair of bromides and in both cases a carbene intermediate is excluded as being involved in the major reaction pathway. *cis*- and *trans*-β-bromostyrene-α-C^{14} have been shown when treated with butyllithium in ether at −35° followed by carbonation to give phenylpropiolic acid still labeled at the carbon atom attached to the phenyl ring. The consequences of these observations are discussed.

In the course of a study[3,4] of the rearrangement with butyllithium of 2,2-diphenylvinyl halides it became necessary to determine the stereochemical course of the reaction. For this purpose *cis*- and *trans*-1-phenyl-1-*p*-chlorophenyl-2-bromoethylene-1-C^{14} (*cis*- and *trans*-I) were prepared. The method of synthesis was as indicated in the formula Chart.

The *cis* and *trans* isomers were separated by distillation and chromatography. Their configurations have been assigned previously by Bergmann, Engel and Meyer[5] on the basis of dipole moment measurements. Reaction of the *cis*-bromide (*cis*-I) with butyllithium in ether solution at −35° and then carbonation gave *p*-chlorodiphenylacetylene (II) (24%) and 45% of *cis*-3-*p*-chlorophenylcinnamic acid (III). Oxidation of the diarylacetylene II gave purified *p*-chlorobenzoic acid which contained 91% of the possible radioactivity. The benzoic



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[1] Taken from the Ph.D. Thesis submitted to the University of Illinois by Edmund W. Flynn, 1956.

[2] Rohm and Haas Fellow, 1954–1955. We are indebted also to E. I. du Pont de Nemours Co., Inc., for a Grant-in-Aid which supported a part of this work.

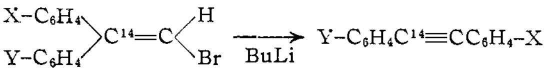
[3] For a preliminary report of a part of the present results see D. Y. Curtin, E. W. Flynn, R. F. Nystrom and W. H. Richardson, *Chemistry & Industry*, 1453 (1957).

[4] D. Y. Curtin and E. W. Flynn, in preparation.

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

acid obtained from the oxidation was not satisfactorily purified.

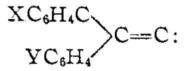
The *trans*-bromide (*trans*-I) still contained an appreciable amount (the infrared spectrum indicated approximately 20%) of *cis*-I. On treatment with butyllithium under the conditions employed with the *cis* isomer, *trans*-I gave an acid mixture (about 30%) not further purified and 26% of the purified chloroacetylene II. Oxidation of II gave *p*-chlorobenzoic acid containing 18% of the possible radioactivity. The major course of each of these reactions is clearly that shown in the following equation; that is, the aryl group *trans* to the bromine atom in I is the group which moves predominantly.



$$\underset{\mathrm{I}}{\mathrm{(X{-}C_6H_4)(Y{-}C_6H_4)C^{14}{=}C(H)Br}} \xrightarrow[\mathrm{BuLi}]{} \underset{\mathrm{II}}{\mathrm{Y{-}C_6H_4C^{14}{\equiv}CC_6H_4{-}X}}$$

I II

While this work was in progress a similar study was reported by Bothner-By[6] of the rearrangement with potassium *t*-butoxide in *t*-butyl alcohol of *cis*- and *trans*-1-*p*-bromophenyl-1-phenyl-2-bromoethylene-1-C.[14] The stereochemical course of the butyllithium rearrangement is the same as that previously reported for the rearrangement with potassium *t*-butoxide. As was pointed out[6] such stereochemical results exclude the possibility that the carbene is an intermediate, at least in the major reaction pathway of each of these reactions.



$$\mathrm{(XC_6H_4C)(YC_6H_4)C{=}C{:}}$$

The reaction of *cis*- and *trans*-β-bromostyrene (*cis*- and *trans*-IV) with lithium reagents to yield lithium phenylacetylide is of interest because of a number of peculiarities which suggest that it might involve initial attack of the lithium reagent at the β-hydrogen atom (α to the bromine) and so would be related to the rearrangement studied in the first part of this paper. The elimination reaction is very rapid only when hydrogen atoms are available on both α- and β-carbon atoms of the olefin unit.[7] The reaction of each of the stereoisomers (*cis*- and *trans*-IV) with phenyllithium in dibutyl ether has been reported by Cristol and Helmreich,[8] since the present work was completed, to be first order in phenyllithium and in vinyl bromide (IV). It is of particular interest that the rate of reaction of the *trans* isomer (*cis* elimination) was 2–6 times that of the *cis* (*trans* elimination) in contrast to their behavior toward alkali in isopropyl alcohol. In view of the ease of rearrangement of 1,1-diaryl-2-bromoethylenes with lithium reagents under comparable conditions, the possibility existed that phenyl migration might be involved in the reaction of the β-bromostyrenes also. *cis*- and *trans*-β-bromostyrene-α-C^{14} (*cis*- and *trans*-IV) were prepared from benzoic acid-7-C^{14} by the route shown below, based on the methods of Grovenstein and Lee[9] and Cristol and Norris.[10]

$$\mathrm{C_6H_5C^{14}OOH} \xrightarrow[\mathrm{SOCl_2}]{} \xrightarrow[\substack{\mathrm{Pd,\ BaSO_4}\\ \text{(Rosenmund)}}]{\mathrm{H_2}}$$

$$\mathrm{C_6H_5C^{14}H{=}O} \xrightarrow[\mathrm{CH_3COOK}]{\mathrm{(CH_3CO)_2O}}$$

$$\begin{tikzcd}
\underset{trans}{\mathrm{C_6H_5C^{14}H{=}CHCOOH}} \arrow[r] & \underset{erythro}{\mathrm{C_6H_5C^{14}HBrCHBrCOOH}} \arrow[d, "\mathrm{OH^-,\ H_2O}"'] \arrow[rd, "\mathrm{NaHCO_3,\ acetone}"] & \\
 & \underset{trans\text{-IV}}{\mathrm{C_6H_5C^{14}H{=}CHBr}} & \underset{cis\text{-IV}}{\mathrm{C_6H_5C^{14}H{=}CHBr}}
\end{tikzcd}$$

Each isomer was allowed to react with one molar equivalent of butyllithium in ether at −35° for 0.5 hr. Carbonation of the reaction mixture from *trans*-IV afforded phenylpropiolic acid in 51% yield and that from *cis*-IV gave phenylpropiolic acid in 26% yield. In each case degradation of the phenylpropiolic acid obtained with acidic potassium permanganate solution gave benzoic acid containing 100% of the theoretical amount of C^{14}. The course of either rearrangement was thus that shown below and involved no phenyl migration.

$$cis\text{- or } trans\text{-IV} \xrightarrow[\mathrm{C_4H_9Li}]{} \xrightarrow[\mathrm{CO_2}]{} \mathrm{C_6H_5C^{14}{\equiv}CCOOH}$$

It seems likely that, as suggested by Cristol and Helmreich,[8] the slow step in the elimination reaction of each of the β-bromostyrenes involves the removal of a proton α to the bromine atom by a molecule of phenyllithium.[11]

Although it is possible that the first proposed intermediate V loses lithium bromide in a second step to give the carbene VI as an intermediate, it

$$\underset{\mathrm{V}}{\mathrm{C_6H_5CH{=}C(Li)Br}} \qquad \underset{\mathrm{VI}}{\mathrm{C_6H_5CH{=}C{:}}}$$

V VI

appears unlikely that VI is an intermediate here since such an intermediate is not important in the reactions of the analogous aryl bromides (*cis*- and *trans*-I).

Experimental[12]

***trans*-Cinnamic Acid Dibromide-3-C^{14}**.—Bromobenzene (2.85 mmoles) was converted to the Grignard reagent and carbonated[13] with carbon dioxide[14] containing C^{14} to give benzoic acid-7-C^{14} which was separated from any neutral products by extraction and then recrystallized from water; when diluted with Merck "reagent-grade" benzoic acid it showed an activity of 10.9 μc./mmole. This was converted to benzoyl chloride-7-C^{14}, b.p. 70–73° (10 mm.), by treatment with thionyl chloride. Benzaldehyde-7-C^{14} (b.p. 62–65°, 10–15 mm.), prepared by Rosenmund reduction[15] of the benzoyl chloride was condensed with acetic anhydride[16] to yield cinnamic acid-3-C^{14} with specific activity

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[6] A. A. Bothner-By, This Journal, **77**, 3293 (1955).

[7] See D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 4519 (1951), for a discussion of this point.

[8] S. J. Cristol and R. F. Helmreich, *ibid.*, **77**, 5034 (1955).

[9] E. H. Grovenstein, Jr., and D. Lee, *ibid.*, **75**, 2639 (1953).

[10] S. J. Cristol and W. P. Norris, *ibid.*, **75**, 2646 (1953).

[11] This step could be concerted with any additional process not involving a second molecule of phenyllithium—such as hydrogen-migration—but since there is no evidence supporting such mechanisms and since they appear to complicate the situation they will not be considered further unless new data require them.

[12] All melting points are corrected. Microanalyses were kindly performed by Mr. Josef Nemeth, Mrs. Maria Benassi, Mrs. Lucy Chang, Mrs. Esther Fett and Mr. Rollo Nesset of the Microanalytical Laboratory of the University of Illinois and by the Clark Microanalytical Laboratory, Urbana, Ill.

[13] H. Gilman and R. H. Kirby, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 361.

[14] Obtained as barium carbonate-C^{14} from the United States Atomic Energy Commission, Oak Ridge National Laboratory, Oak Ridge, Tenn.

[15] C. Weygand and W. Meusel, *Ber.*, **76**, 503 (1943).

[16] J. R. Johnson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 248.

10.6 μc./mmole. (The theoretical activity based on starting benzoic acid is 10.9 μc./mmole.) The acid (after dilution with an equal amount of unlabeled acid) was converted to the dibromide by treatment with bromine in carbon disulfide solution.[17] The dibromide-3-C^{14} (80% yield) so obtained had m.p. 200–201°.

p-Chlorobenzophenone-1-C^{14}.—Benzoyl chloride-7-C^{14} (48.9 g., 0.35 mole), prepared from benzoic acid-7-C^{14} with an activity of 7.05 μc./mmole, was treated with chlorobenzene (42.8 g., 0.35 mole) and aluminum chloride (48.9 g., 0.35 mole) by the method of Fieser for benzoylnaphthalene.[18] A 70% yield (53 g.) of *p*-chlorophenone-1-C^{14}, m.p. 76–77° (lit.[19] m.p. 75°), specific activity 7.05 μc./mmole, was obtained. The product was diluted with 153 g. of *p*-chlorobenzophenone (Dow Chemical Co. product, m.p. 78–79°) by solution in 1 l. of ether and distillation of the ether to give ketone with a specific activity of 1.64 μc./mmole (calcd. 1.72 μc./mmole).

***cis*- and *trans*-1-Phenyl-1-*p*-Chlorophenyl-2-bromoethylene-1-C^{14}** (*cis*- and *trans*-I).—Addition of methylmagnesium iodide to the *p*-chlorobenzophenone-1-C^{14} (216 g.) described above and then dehydration with 300 ml. of 20% sulfuric acid gave 103 g. (47%) of 1-phenyl-1-*p*-chlorophenylethylene-1-C^{14}, b.p. 153–158° (10 mm.). Addition of a 6% excess of bromine (80 g.) in carbon tetrachloride followed by distillation gave 125 g. (0.42 mole, 89%) of I, b.p. 145–160° (0.5 mm.). The product was fractionally distilled to yield (from the last fraction) 14.8 g. of liquid, b.p. 165–170° (0.5–1.0 mm.), which was crystallized from ethanol and low boiling petroleum ether to give 5.0 g. of *cis*-I (*p*-chlorophenyl group and bromine atom *cis*), m.p. 88–89° (lit.[5] 92–93°), specific activity 1.70 μc./mmole.

Anal. Calcd. for $C_{14}H_{10}BrCl$: C, 57.27. Found: C, 57.30.

Purification of an 11-g. center cut, b.p. 155–157° (0.5–1.0 mm.), from the distillation above by chromatography on alumina gave a liquid fraction (6.8 g.) believed to be essentially *trans*-I, specific activity 1.72 μc./mmole (lit.[5] m.p. 43–44°). On the basis of the absorption at 725 cm.$^{-1}$ where *cis*-I has strong absorption it was estimated that not more than 20% of *cis*-I could have been present.

Anal. Calcd. for $C_{14}H_{10}BrCl$: C, 57.27. Found: C, 57.25.

Reaction of *cis*- and *trans*-I with Butyllithium.—*cis*-I (5.00 g., 17 mmoles) in 100 ml. of anhydrous ether at −35° in an atmosphere of nitrogen was treated with a 10% excess over one equivalent (26.5 ml.) of a titrated butyllithium solution and the temperature held at −35 to −20° for 0.5 hr. The reaction mixture was then allowed to warm to room temperature and neutralized with 50 ml. of 20% hydrochloric acid. Separation of the neutral fraction by extraction with ether followed by drying over anhydrous sodium sulfate and removal of the ether gave a residue of 2.24 g. Purification by chromatography on alumina yielded 0.880 g. (4.13 mmoles) of *p*-chloro-(diphenylacetylene II), m.p. 82–83°, specific activity 1.68 μc./mmole. Oxidation of 0.880 g. in 50 ml. of pyridine with 40 ml. of aqueous potassium permanganate (4 g.) containing 1 ml. of 10% sodium hydroxide under reflux for 4 hr. gave 540 mg. of solid acids after removal of most of the solvent, extraction of any neutral products with ether and precipitation with hydrochloric acid. By fractional crystallization of the product was obtained 210 mg. of *p*-chlorobenzoic acid, m.p. 241–242°, activity 1.54 μc./mmole. The activity was thus 91% of that present in the original bromide *cis*-(I).

Anal. Calcd. for $C_7H_5ClO_2$: C, 53.8; Cl, 22.7. Found: C, 53.5; Cl, 22.6.

Only impure benzoic acid (50 mg., m.p. 116–118°, activity 0.38 μc./mmole) could be obtained. This radioactivity corresponds to 22% of that present in the original bromide.

Anal. Calcd. for $C_7H_6O_2$: C, 68.9. Found: C, 65.2; Cl, 1.7.

From the base-soluble fraction obtained from the original carbonation mixture on acidification was precipitated a solid which after recrystallization from ethanol gave 1.96 g. (45%) of ***cis*-β-*p***-chlorophenylcinnamic acid, m.p. 177–178° (lit.[20] "α," m.p. 172°; "β," m.p. 165–166°; mixture, m.p. 140°).

trans-I, on treatment with butyllithium under conditions similar to those used for *cis*-I above gave 0.950 g. (0.446 mmole) of II, m.p. 82–83°, specific activity 1.72 μc./mmole, and 1.67 g. of crude acids, m.p. 130–168°, which were not examined further. The diacylacetylene II (0.95 g.) oxidized as was that obtained from *cis*-I gave 0.20 g. of *p*-chlorobenzoic acid, m.p. 240–242°, radioactivity 0.31 μc./mmole or 18% of that in the original bromide. No purified benzoic acid could be isolated.

Anal. Calcd. for $C_7H_5ClO_2$: C, 53.8. Found: C, 53.7.

***trans*-β-Bromostyrene-2-C^{14}** (*trans*-IV) was prepared from 19.5 g. (64 mmoles) of cinnamic acid dibromide-3-C^{14} by the method of Grovenstein and Lee.[9] Distillation of the product gave 4.61 g. (45%), b.p. 50–52° (0.5 mm.), n^{25}_D 1.6059.

cis-IV was prepared from 19 g. (64 mmoles) of cinnamic acid dibromide-3-C^{14} by the method of Cristol and Norris.[21] Distilled *in vacuo*, it amounted to 6.07 g. (59%), b.p. 37–39° (0.5 mm.), n^{20}_D 1.5995.

Reaction of *trans*-IV with Butyllithium.—*trans*-IV (4.75 g., 26 mmoles) in 75 ml. of anhydrous ether at −35° was treated with butyllithium (10% excess over two molar equivalents titrated in 77 ml. of ether) which was added over a period of 15 min. The temperature rose slightly during the addition but was held at −35° for 0.5 hr. thereafter and the reaction mixture was then poured onto an excess of powdered solid carbon dioxide. Separation of the acidic fraction of the product gave 1.93 g. (51%) of phenylpropiolic acid, m.p. 136–137°, which was purified by recrystallization from carbon tetrachloride and which was the only product isolated. *cis*-Bromostyrene-2-C^{14} (4.83 g., 26 mmole) treated similarly gave 0.99 g. (26%) of phenylpropiolic acid, m.p. 136–137°, as the only acidic product.

The phenylpropiolic acid (0.494 g., 3 mmole) from *trans*-IV was oxidized with potassium permanganate (3 g.) in 20 ml. of water containing 2 ml. of concentrated sulfuric acid by warming on a steam-bath for 5 min. There resulted benzoic acid (0.215 g., 52%), m.p. 122–122.5° (purified by recrystallization from water), with a specific activity of 2.46 μc./mmole. (The theoretical specific activity is 0.40 based on the dilution of benzoic and cinnamic acids having specific activities of 10.9 and 10.6 μc./mmole, respectively.)

Similar oxidation of the phenylpropiolic acid from *cis*-IV gave 0.166 g. (35%) of benzoic acid, m.p. 122–122.5°, with a specific activity of 3.19 μc./mmole. (The theoretical value, based on the dilution of benzoic acid and cinnamic acid having specific activities of 10.9 and 10.6 μc./mmole, is 3.06.)

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[17] A. Michael, *Ber.*, **34**, 3663 (1901).

[18] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., p. 194.

[19] P. J. Montague, *Rec. trav. chim.*, [2] **26**, 253 (1907).

[20] F. Bergmann, W. Weizmann, E. Dimant, J. Patai and J. Szmuszkowicz, THIS JOURNAL, **70**, 1612 (1948).

[21] S. J. Cristol and W. P. Norris, *ibid.*, **75**, 2646 1953).