at the surface. No material appeared in any of the fractions excepting that in the petroleum ether–ether 1:1 solvent (171 mg.) and that in the ether solvent (15 mg.). These two combined fractions (186 mg., 82% recovery), m.p. 22–24°, $n^{25}\mathrm{D}$ 1.4702, were taken as pure *dl*-ricinoleic acid.

Anal. Calcd. for $C_{18}H_{34}O_3$: C, 72.4; H, 11.5; neut. equiv., 298.5. Found: C, 72.2; H, 11.3; neut. equiv., 298.1.

This synthetic ricinoleic acid showed intense hydroxyl absorption at 3401 cm.$^{-1}$ (2.94 μ) and carbonyl absorption at 1715 cm.$^{-1}$ (5.83 μ). The infrared absorption curve for this material had all the features of the curve for natural ricinoleic acid (see below), although the three minor peaks at 9.0–9.5 μ differed slightly in relative intensity. The melting points reported before for *dl*-ricinoleic acid are 23–24°[2] and 23–24.5°.[4] The index of refraction may be compared to the $n^{25}\mathrm{D}$ 1.4698 value observed in this work (see below) for natural ricinoleic acid, and to the recorded values of $n^{19}\mathrm{D}$ 1.4723[2] and $n^{25}\mathrm{D}$ 1.4702[4] for racemic ricinoleic acid.

Natural Ricinoleic Acid.—Lithium ricinoleate,[23] m.p. 181–182.5°, was shaken vigorously for 15 min. with 50 ml. of ether and 50 ml. of ice-cold 5% hydrochloric acid. The separated aqueous phase was extracted with two 25-ml. portions of ether, and the combined ethereal solutions were washed free of mineral acid with water and were dried over sodium sulfate. The yellow oil (4.2 g.) remaining after removal of solvent at room temperature at reduced pressures showed m.p. 4–8° and $n^{25}\mathrm{D}$ 1.4673. This material was purified by chromatography as described for the synthetic material. The resulting refined ricinoleic acid, m.p. 20–22°, $n^{25}\mathrm{D}$ 1.4698, neut. equiv. 298.8, was obtained in 67% yield from the lithium salt.

Methyl *dl*-Ricinoleate.—A distilled ethereal solution of diazomethane, taken in excess, was added slowly to an ice-cold solution of 1.0 g. (0.003 mole) of unpurified *dl*-ricinoleic acid, $n^{25}\mathrm{D}$ 1.4676. The yellow reaction mixture was swirled and allowed to stand overnight at room temperature. After addition of one drop of acetic acid, the solution was washed with three 20-ml. portions of water and then dried with sodium sulfate. Ether was removed, and the yellow residue was distilled in a short-path still formed from a creased test-tube. The initial distillate, $n^{25}\mathrm{D}$ 1.4610, collected at bath temperature 155–157° (0.01 mm.), weighed 0.99 g. The colorless distillate from the second distillation weighed 0.75 g. and showed $n^{25}\mathrm{D}$ 1.4608. A sample for analysis was taken from the third distillate, $n^{25}\mathrm{D}$ 1.4603, b.p. (bath temperature) 164–166° (0.02 mm.), which weighed 0.60 g.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.0; H, 11.6. Found: C, 72.9; H, 11.5.

Methyl ricinoleate[23] from castor oil distilled at a bath temperature of 161–164° (0.02 mm.) and showed $n^{25}\mathrm{D}$ 1.4602. The infrared spectra of synthetic and of castor oil methyl ricinoleate were superposable, both curves showing hydroxyl (3448 cm.$^{-1}$ or 2.90 μ) and carbonyl (1745 cm.$^{-1}$ or 5.73 μ) peaks. Methyl *dl*-ricinoleate has been reported before with $n^{20}\mathrm{D}$ 1.4632[4] and $n^{16}\mathrm{D}$ 1.4638.[2]

Methyl *dl*-12-Hydroxystearate (IX).—Methyl *dl*-ricinoleate (1.77 g. or 0.0060 mole), glacial acetic acid (25 ml.) and platinum oxide (0.20 g.) were stirred at room temperature under an atmosphere of hydrogen. The calculated amount of hydrogen was absorbed within 25 min., after which time hydrogen uptake stopped. The catalyst was removed by filtration, and the solvent by distillation at room temperature at reduced pressures. An ether solution of the residue was washed repeatedly with 20-ml. portions of water until the washings were neutral to litmus, and then was dried with sodium sulfate. The crystalline solid (1.50 g., m.p. 53–53.5°) remaining after removal of solvent *in vacuo* at room temperature was crystallized from acetone to give methyl *dl*-12-hydroxystearate (1.37 g., 77%), m.p. 55–55.5°. Two additional crystallizations from acetone did not change the melting point.

Anal. Calcd. for $C_{19}H_{38}O_3$: C, 72.6; H, 12.2. Found: C, 72.4; H, 12.3.

The same racemic material was reported before with m.p. 50–51°,[24] and m.p. 53.4–53.6°.[25] The optically active form has m.p. 57.5–58°.[26]

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[23] We are indebted to The Baker Castor Oil Co. for providing this material.

[24] C. G. Tomecko and R. Adams, This Journal, **49**, 522 (1927).

[25] S. Bergström, G. Aulin-Erdtman, B. Rolander, E. Stenhagen and S. Östling, *Acta Chem. Scand.*, **6**, 1157 (1952).

[26] F. Straus, H. Heinze and L. Salzman, *Ber.*, **66**, 631 (1933).

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, SCHOOL OF PHARMACY, THE HEBREW UNIVERSITY, HADASSAH MEDICAL SCHOOL]

The Stereochemistry and Mechanism of Reversible Polymerization of 2,2-Disubstituted 1,3-Propanediol Carbonates

BY SHALOM SAREL[1] AND LEO A. POHORYLES

RECEIVED JANUARY 25, 1958

The effect of alkyl substituents positioned at carbon atoms 1 and 2 in 1,3-propanediol carbonates upon their tendencies to undergo reversible polymerization is described. Polyneopentylene carbonate displays thermal transformation in the solid state. A tentative spiral structure having a six-membered ring fold is proposed for the polymer chain. The existing physical and chemical properties of the polymeric material can reasonably be correlated with the structural picture presented. The stereochemical course and mechanism of reversible polymerization are discussed.

Introduction

In the course of synthetic work aimed at preparing some cyclic carbonates of 2,2-disubstituted 1,3-propanediols (I), needed for another research program,[2] we observed that, depending on reaction conditions and molecular structure, some carbonates are obtained only in a polymeric form (II). Thus, when 2,2-dimethyl-, 2-methyl-2-*n*-propyl- and 2-methyl-2-isoamyl-1,3-propanediol are treated with diethyl carbonate in the presence of catalytic amounts (0.5% mole) of sodium methoxide, only polycarbonates (IIb-IId) are produced in high yield. On the other hand, six-membered cyclic carbonates (Ie-If) are exclusively produced when 2,2-diethyl-, 2-ethyl-2-phenyl-1,3-propanediol and 2,4-pentanediol and 1,3-butanediol are subjected to the above ester-interchange reaction conditions.[3] Compounds Ib, Ic and Id, also could be obtained by using larger amounts of catalyst (2.5%–5% mole) and controlling the elimination of ethanol produced during the above-mentioned ester-interchange reaction, or through thermal depolymerization of the polymeric products. Compound IIb, in analogy

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[1] Formerly Shalom Israelashvili.

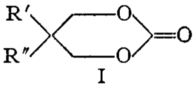
[2] L. A. Pohoryles and S. Sarel, *Compt. rend.*, **245**, 2321 (1957).

[3] L. A. Pohoryles and S. Sarel, manuscript in preparation.

with IIa,[4] is a crystalline product having a higher melting point than IIa, while IIc and IId are viscous liquids which are undistillable, without skeletal disintegration, even in high vacuum.

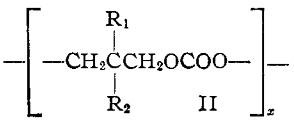
The information now at hand suggests that the presence of methyl substituents at 1, and ethyl substituents at carbon atom 2, in 1,3-propanediols does not favor the formation of polymeric carbonates (II). However the introduction of methyl groups at carbon atom 2 has little or no effect in this respect.

We wish to report herein the results of a study of the formation, structure and some physical and chemical properties of the polymeric neopentylene carbonates (IIb). This study was carried out with the purpose of acquiring a more intimate insight into the effect of branching upon the ability of six-membered cyclic carbonates to undergo reversible polymerization–depolymerization conversion.[5]



I

Ia, IIa, $R_1 = R_2 = H$; $x = 38\text{–}45$
Ib, IIb, $R_1 = R_2 = Me$; $x = 20\text{–}22$
Ic, IIc, $R_1 = Me$, $R_2 = n\text{-Pr}$; $x = 14\text{–}15$



$$-\left[-CH_2\overset{R_1}{\underset{R_2}{C}}CH_2OCOO-\right]_x-$$

II

Id, IId, $R_1 = Me$, $R_2 = i\text{-Am}$
Ie, $R_1 = Et$
If, $R_1 = Et$, $R_2 = Ph$

Experimental

Preparation of Polymeric 2,2-Dimethyl-1,3-propanediol Carbonate (IIb).—A mixture of 20.8 g. (0.2 mole) of neopentyl glycol,[6] 24 g. (0.2 mole) of diethyl carbonate and 0.05 g. of dry sodium methoxide[7] was placed in a flask equipped with a 36-inch Vigreux column. The mixture was heated gradually and the ethanol formed in the course of the reaction was distilled off at 77–84°. At the end, excess of reactants was removed by distillation at reduced pressure. The residue (25 g.), when melted and then cooled, yielded an opaque, glassy and tough material. From the melt, rubber-like fibers could be drawn. It could not be sublimed or distilled in high vacuum at a bath temperature of 200°. The glassy mass after trituration and crystallization from ligroin-benzene yielded 23.5 g. (90%) of a white powder, m.p. 107–109°.

Anal. Calcd. for $(C_6H_{10}O_3)_x$: C, 55.3; H, 7.7. Found: C, 55.4; H, 7.7; mol. wt., 2500 (calcd. from an intrinsic viscosity of 0.035 by the method of Staudinger[8]).

Compound IIb is insoluble in most organic solvents, but is soluble in benzene. When a sample of 0.5 g. was suspended in 20 ml. of 1 *N* aqueous ethanolic sodium hydroxide and refluxed for 2–3 hours, the starting material was recovered unchanged.

Experiments aimed at establishing hydroxyl end-groups gave negative results. Thus when IIb was treated either with phenyl isocyanate or acetic anhydride-pyridine mixture, only the starting material was recovered unchanged.

Monomeric Neopentylene Carbonate (Ib).—A mixture of 20.8 g. (0.2 mole) of neopentyl glycol, 30 g. (0.25 mole) of diethyl carbonate and 0.25–0.5 g. (0.005–0.01 mole) of dry sodium methoxide was placed in a distillation apparatus as described above. The mixture was heated (external temperature was 150–160°) and the ethanol which was formed distilled at 78–85°. After two hours, at which time the internal temperature reached to 130°, excess of diethyl carbonate was removed by distillation at reduced pressure. The residue was taken up in benzene, washed with water, dried, and the solvent removed. Distillation at reduced pressure yielded 22–23.5 g. (85–90%) of Ib, b.p. 122° at 2 mm., m.p. 107°. White crystals melting at 110°,[9] were obtained either after sublimation *in vacuo* or by recrystallization from benzene–ligroin.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.39; H, 7.69; mol. wt., 130. Found: C, 55.50; H, 7.70; mol. wt., 132 (Rast).

Thermal Depolymerization of II.—When IIb was heated in a distilling flask by means of direct bunsen flame, the melted product did not show any change in color or even slight charring. Instead, a sudden distillation of colorless product took place, b.p. 279–280° (680 mm.), which upon cooling gave a solid mass. Recrystallization from benzene–ligroin yielded Ib as white crystals, m.p. 109–110°. This upon mixing with IIb gave a depression in melting point. Infrared spectra[10] and mixed melting point determination showed the identity of Ib with an authentic sample prepared by the method of Ludwig and Piech.[9]

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.39; H, 7.69; mol. wt., 130. Found: C, 55.48; H, 7.72; mol. wt., 138 (Rast).

Monomeric and Polymeric 2-Methyl-2-*n*-propyl-1,3-propanediol Carbonates (Ic and IIc).—Transesterification of 2-methyl-2-*n*-propyl-1,3-propanediol with diethyl carbonate using 5% mole of dry sodium methoxide in a fashion described above yielded the cyclic monomer Ic, b.p. 117–119° at 2 mm., $n^{20}D$ 1.4540, in 60% yield.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.76; H, 8.88. Found: C, 60.78; H, 9.2.

In the distillation flask a residue of a viscous polymeric product remained (IIc), $n^{20}D$ 1.4650, which amounted to 25% yield.

Anal. Calcd. for $(C_8H_{14}O_3)_x$: C, 60.7; H, 8.9. Found: C, 60.2; H, 9.1; av. mol. wt., 2500 (calcd. from an intrinsic viscosity of 0.0284[8]).

When the foregoing ester interchange reaction was performed in the presence of smaller amounts of sodium methoxide (around 0.5% mole) a variety of polycarbonates were obtained. Their molecular weights ranged between 400–3000, depending on the amount of catalyst and reaction conditions.

Thermal Depolymerization of IIc.—The depolymerization of IIc into Ic was effected in 70% yield by heating the product by means of a direct bunsen flame in the presence of catalytic amounts of dry sodium methoxide as described. The cyclic monomer distilled off at 240° (680 mm.), $n^{20}D$ 1.4510, leaving behind some charred product.

Anal. Found: C, 61.20; H, 9.2.

Thermal Transformation in Solid IIb.—When IIb was heated for one week in an oven of constant temperature (at 100 ± 1°) its melting point was continuously increased from 107–109° (α-form) to 117–119° (β-form). The conversion of β- to α-form could be effected either by recrystallization from benzene–ligroin or melting and then cooling of the product. Repeating the conversion process several times apparently does not involve changes in the degree of polymerization. The X-ray powder diagrams of both forms were determined by exposing materials to copper Kα radiation on a Guinier camera for eight hours. In each form two distinct lines were obtained. They were related to interplanar spacings of 5.1 and 4.9 Å. for the α-form and 5.0 4.8 Å. for the β-form. The X-ray analysis of Ib demonstrates the presence of an interplanar spacing of 4.9 ± 0.2 Å. (very strong).[11]

The infrared spectra of solid materials were determined on a Perkin-Elmer double beam, model 21, recording infrared spectrophotometer from 650 to 5000 cm.$^{-1}$, using pressed

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[4] W. H. Carothers and F. J. Van Natta, THIS JOURNAL, **52**, 314 (1930).

[5] (a) W. H. Carothers, G. L. Dorough and F. J. Van Natta, *ibid.*, **54**, 761 (1932); (b) W. H. Carothers, *Chem. Revs.*, **8**, 353 (1931).

[6] Supplied by Eastman Kodak Co.

[7] A product of Mathieson Chemical Corp.

[8] W. T. Smith and R. L. Shriner, "The Examination of New Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 71.

[9] B. J. Ludwig and E. C. Piech, THIS JOURNAL, **73**, 5779 (1951), reported a m.p. 110–111°.

[10] L. A. Pohoryles and S. Sarel, *Bull. Research Council Israel*, **7A**, 42 (1957).

[11] This could be assigned to the repeating unit of the six-membered ring of the cyclic carbonate.

potassium bromide pellets. The results are given in Table I.

TABLE I

INFRARED ABSORPTION BANDS (CM.$^{-1}$) OF POLYMERIC AND MONOMERIC NEOPENTYLENE CARBONATES

	C–H scissoring bending[12]		C–O (ethers)		
α-Form	1397	1385	1050	1022	972s.
β-Form	1410	1395sh.	1038	1015sh.	965s.
Ib	1412	1380	1040	1008	958w.

Results and Discussion

The experimental evidence clearly indicates that branching at carbon atom 2 of the diol moiety has an effect upon both the length[13] and the tendency of the polymeric chain to undergo depolymerization reaction. The characteristic property of the six-membered cyclic ester to undergo reversible polymerization is entirely lost upon introducing ethyl substituents at carbon 2 of the diol moiety. Kinetic factors could not possibly account for this, as it already has been shown that Ib and If are hydrolyzed by bases approximately at the same rate as Ia.[2,14] The peculiar point is that the ability to undergo polymerization persists as long as one of the substituents on carbon atom 2 is a methyl group (compare Ic and Id). This suggests that the conformation assumed by alkyl substituents in Ic, Id, Ie and If affects the tendency to undergo such a process. Axial methyls in Ib-Id apparently have no determining effect compared with axial ethyls in this respect.

On the other hand, the ease of depolymerization can probably be related to the molecular configuration adopted by the polymeric chain. As a convenient hypothesis it would be most plausible to assume a folded structure for the polymeric chain, as illustrated by the α-helix common to certain synthetic and natural macromolecules.[15] This folded structure is to be expected from the known effect of side chains upon the stable configuration of the main polymer chain[16] and from the peculiar solubility of IIa-IId in benzene.[17] The presence of the same interplanar spacing of 4.9 ± 0.2 Å. both in the monomeric and polymeric forms suggests a six-membered ring fold for the polymer chain.[11] Such an arrangement would be maintained by the dipole–dipole interactions[4,18] between O-atoms of one O–CO–O group with the CO of such a vicinal group along the chain (see Fig. 2). The resulting six-membered ring fold conceivably adopts the chair conformation. This is deduced from minimization of non-bonded interactions which refers ideally to isolated six-membered cyclic ester molecules as well as to molecules in the crystal.[19]

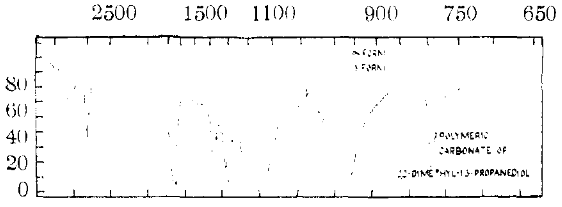

Fig. 1.—Infrared spectrogram of α- and β-forms of polyneopentylene carbonates.

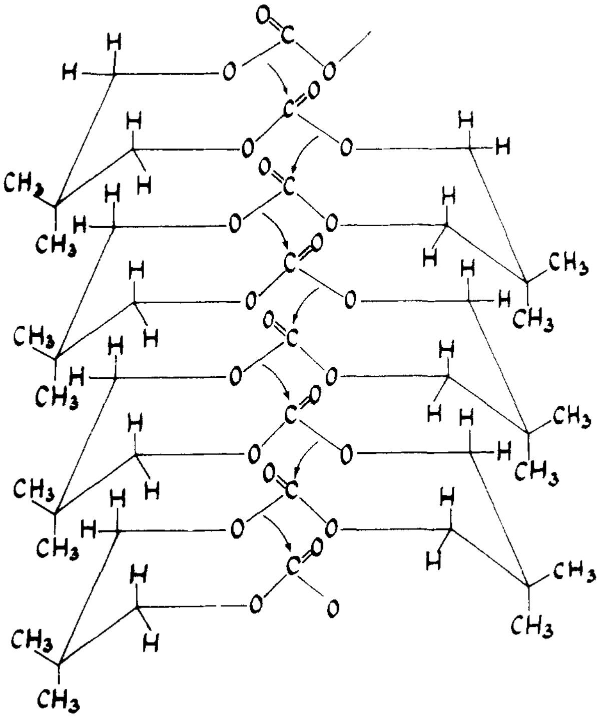

Fig. 2.—A schematic planar representation of the six-membered ring fold of IIb. The curved arrow indicates the mode of O–CO bond interchange along polymer chain.

Thermal Transformation.—The physical data at hand suggest that α- and β-forms (see Experimental) are actually polymorphs.[20] The X-ray powder diagrams indicate that the thermal transformation involves a change in the packing of the crystal into shorter spacings having a higher degree of sym-

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(12) R. N. Jones and C. Sandorfy in Weissberger's "Technique of Organic Chemistry," Vol. 9, Interscience Publishers, Inc., New York, N. Y., 1956, p. 344.

(13) For IIb, 20–22 structural units of $-CH_2CR_1R_2CH_2OCO-$ are found as compared to 38–45 units reported for IIa. The same effect has been observed also for the lengthening of the chain of this unit (ref. 4).

(14) *meso*-Hydrobenzoin carbonate (the phenyls are *cis*), although it is hydrolyzed by alkali approximately at the same rate as Ia and IIa,[2] still displays the same inability to undergo reversible polymerization reaction shown by a variety of five-membered cyclic esters. This stands in contrast to the interpretation suggested by Carothers,[5a] who accounted for the foregoing property of the five-membered cyclic esters predominantly by kinetic factors.

(15) For more fully documented accounts of certain aspects of the problem see E. J. Ambrose in Klyne, "Progress in Stereochemistry," Vol. I, Butterworths Scientific Publications, London, 1954, chapter VII.

(16) In case of polyisobutene it has already been shown that due to the steric effects exerted by the methyl groups, the main polymeric chain possesses a spiral structure; see C. S. Fuller, C. J. Frosch and N. R. Pape, THIS JOURNAL, **62**, 1905 (1940).

(17) Some polypeptides in the folded form were readily soluble in non-polar solvents such as benzene, whereas the same polymers when transformed into the extended form were completely insoluble. See C. H. Bamford, W. E. Hanby and F. Happey, *Proc. Roy. Soc.* (*London*), **A206**, 407 (1951).

(18) B. A. Arbuzov and T. G. Shavsha, *Doklady Akad. Nauk SSSR*, **68**, 1045 (1949); *C. A.*, **44**, 886 (1950); J. L. Hales, J. I. Jones and W. Kynaston, *J. Chem. Soc.*, 622 (1957).

(19) For leading references, see D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 44 (1956); E. L. Eliel in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 126.

(20) For an excellent review of thermal transformations, see A. R. Ubbelohde, *Quart. Revs.*, **11**, 246 (1957).

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.

JERUSALEM, ISRAEL

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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]

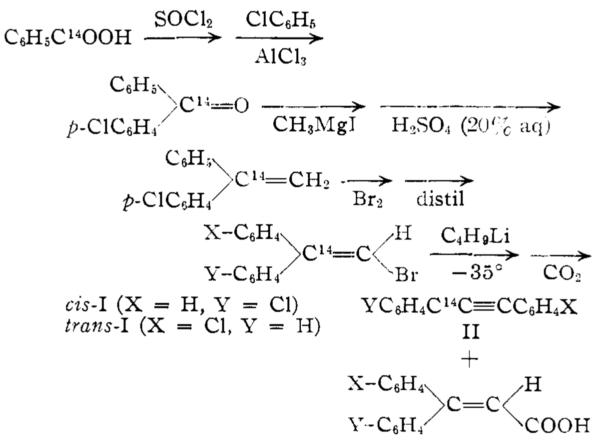
BY DAVID Y. CURTIN, EDMUND W. FLYNN[2] AND ROBERT F. NYSTROM

RECEIVED APRIL 3, 1958

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).