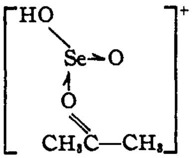
ity =  where the acetone has displaced a hydroxyl ion from the selenium. In favor of this structure, one may cite the complete agreement with the kinetic evidence; but also, the subsequent disproportionation of the intermediate to pyruvaldehyde and selenium is most reasonable. The coördination of the acetone through its oxygen necessarily results in a redistribution of charge within the acetone molecule which would result in enhanced reactivity of the α-hydrogens; and it is not unlikely that the bond distances and angles in the complex are such that the selenium oxygens are placed in a favorable steric position for reaction with α-carbon.

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Iodometric Analysis of *o*-Nitrobenzeneseleninic Acid

BY OLAV FOSS

o-Nitrobenzeneseleninic acid has been found to react with thiosulfuric acid as follows

$$o\text{-}O_2NC_6H_4Se(O)OH + 3S_2O_3^{--} + 3H^+ = o\text{-}O_2NC_6H_4SeS_2O_3^- + S_4O_6^{--} + 2H_2O$$

The reaction is rapid and quantitative. The reaction product, *o*-nitrobenzeneselenenyl thiosulfate, has previously been isolated as a potassium salt by the reaction of *o*-nitrobenzeneselenenyl bromide with potassium thiosulfate,[1] and is also formed in reactions of various *o*-nitrobenzeneselenenyl sulfur compounds with thiosulfate.[1] It forms yellowish green, stable solutions. In neutral and acid solutions it is indifferent to iodine and does not interfere with iodine–thiosulfate titrations carried out in the same solutions. Hence the above reaction may be utilized for the iodometric analysis of *o*-nitrobenzeneseleninic acid, excess of thiosulfate being back-titrated with iodine. The following procedure may be employed.

To 12–20 mg. of *o*-nitrobenzeneseleninic acid dissolved in 25 ml. of water are added 5 ml. of 0.1 *N* sulfuric acid and then 20–30 ml. of 0.01 *N* sodium thiosulfate (5 ml. excess). After standing for two to three minutes at room temperature, starch is added, and the excess of thiosulfate is back-titrated with 0.01 *N* iodine.

Notice may be made to the analogous method of Norris and Fay[2] for the iodometric analysis of selenious acid, by means of the change

$$SeO_2 + 4S_2O_3^{--} + 4H^+ = Se(S_2O_3)_2^{--} + S_4O_6^{--} + 2H_2O$$

Experimental

The *o*-nitrobenzeneseleninic acid employed was prepared from the trichloride by hydrolysis,[3] and recrystallized from water until colorless.

0.1589 g. of the acid was dissolved to 250 ml. in water in a volumetric flask. Twenty-five ml. was pipetted out and 5 ml. 0.1 *N* sulfuric acid and then 25 ml. 0.01 *N* sodium thiosulfate (consuming 24.79 ml. of 0.01078 *N* iodine) were added. The time of standing was 2, 2, 5, 5, 8, 8 minutes. Amounts of 0.01078 *N* iodine then consumed: 5.95, 5.92, 5.92, 5.93, 5.92, 5.93 ml., respectively. Average: 5.93 ml., which gives 0.1585 g. of *o*-nitrobenzeneseleninic acid, *i.e.*, 99.7%.

Indifference of *o*-nitrobenzeneselenenyl thiosulfate to iodine. To 25 ml. of 0.01 *N* sodium thiosulfate were added 5 ml. 10% acetic acid, 5 ml. of starch solution, and (a) 20 ml. of water, (b) 20 ml. of 0.01 *M* potassium *o*-nitrobenzeneselenenyl thiosulfate. The solutions were then titrated with 0.01 *N* iodine. Amounts consumed: (a) 24.49, 24.50 ml. (b) 24.50, 24.50, 24.49 ml.

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(1) Foss, THIS JOURNAL, **69**, 2236 (1947).

(2) Norris and Fay, *Am. Chem. J.*, **18**, 703 (1896); **23**, 119 (1900).

(3) Behaghel and Seibert, *Ber.*, **66**, 708 (1933).

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Mixed Crystal Formation in Linear Copolyesters

BY C. S. FULLER

Slagle and Ott[1] showed that solidified mixes of normal aliphatic acids frequently exhibit a single X-ray spacing along the direction of the molecule axes in the mixed crystal. The purpose of this note is to point out that an analogous behavior occurs in copolymers in which the constituents are ethylene glycol dibasic acid residues of different chain lengths and, presumably, are randomly distributed along the long chain molecules.

A copolyester capable of being cold drawn into strong fibers was prepared by treating equal molar quantities of pure 10-, 11- and 12-membered aliphatic dicarboxylic acids with ethylene glycol. The X-ray fiber diagram of the copolymer (Fig. 1 (a)) is similar to that exhibited by many simple linear polyesters.[2] A mixed crystal is therefore indicated.

The average fiber period for the copolyester measures 17.83 Å. This value was obtained from the three strongest layer-line reflections (17.78, 18.00, 17.70). The fiber periods of the constituent ethylene polyesters prepared from the individual pure dibasic acids according to the same procedure are as follows

Ethylene decane 1-10 polyester	16.86 Å.
Ethylene undecane 1-11 polyester	36.32 (18.16 Å.)
Ethylene dodecane 1-12 polyester	19.40 Å.

The odd number of chain atoms in the 1-11 polyester causes a doubling of the fiber period. In addition, as the fiber pattern of Fig. 1b shows, the polar layers are perpendicular to the fiber axis unlike the even polyesters in which these planes are inclined to the axis.[3] It is noteworthy that (insofar as we can speak of polar layers in the copolymer) the pattern of the copolyester exhibits

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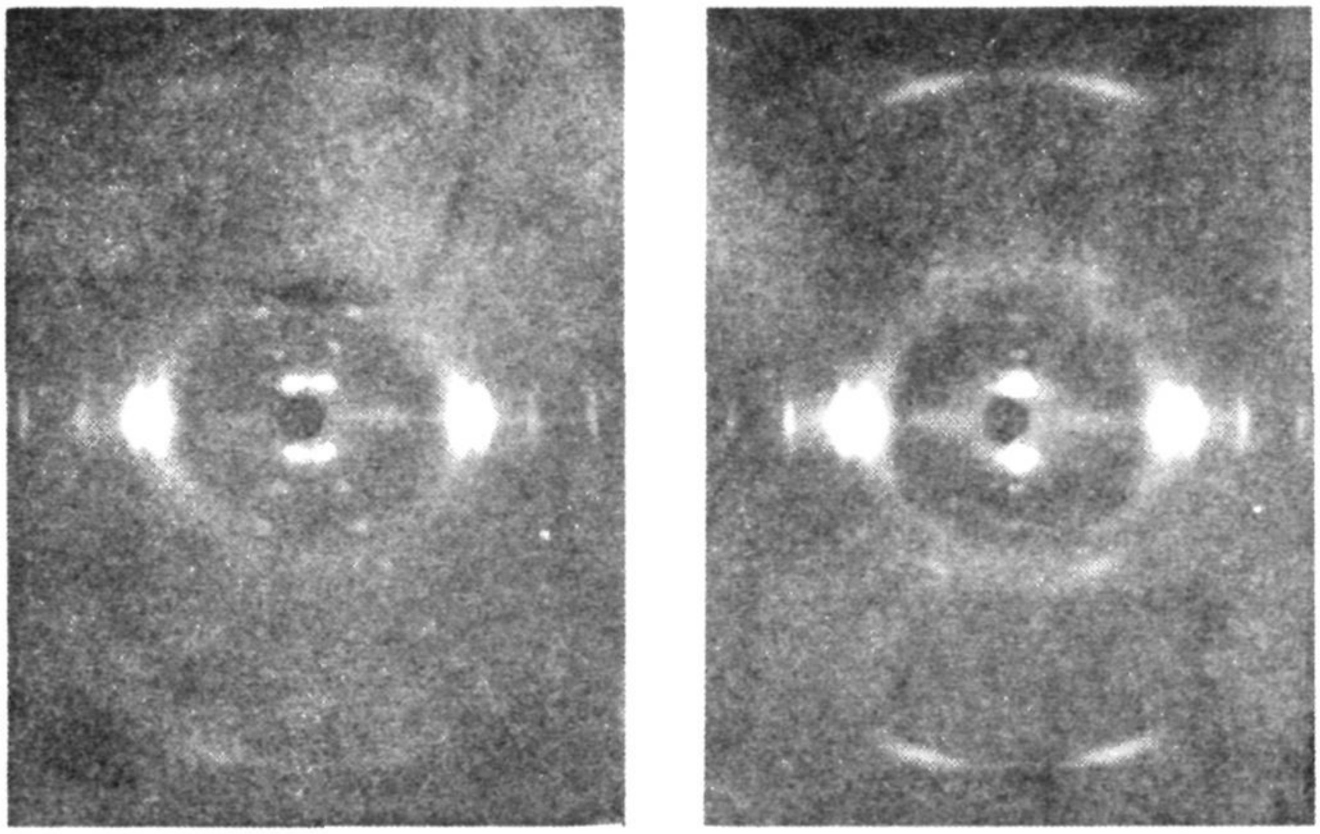
(1) Slagle and Ott, THIS JOURNAL, **55**, 4396 (1933).

(2) Carothers and Hill, *ibid.*, **54**, 1579 (1932).

(3) Fuller and Frosch, *J. Phys. Chem.*, **43**, 323 (1939).



(a) Ethylene 10,11,12 copolyester. (b) Ethylene 11 polyester.

Fig. 1.—X-Ray fiber patterns of ethylene 10,11,12 dibasic acids copolyester (a) and ethylene 11 dibasic acid polyester (b). Fiber axes vertical. Photographs have been retouched to assist reproduction.

layer-line reflections corresponding to *inclined* polar layers.

The fiber period of 17.83 Å. observed for the copolyester is somewhat lower than the value (18.03) obtained by averaging the three repeating lengths of the pure polyesters (19.40, 18.16, 16.84). However, it seems unlikely that an accuracy of greater than ±0.15 Å. can be expected in these measurements. Consequently, for the purposes of the present work the observed fiber period of the copolyester may be considered to be the same as the average of the lengths of the units which have been put into the copolymer.

The presence of pyramidal rather than meridian reflections in the copolyester indicates a preponderance of the staggered over the horizontal type of packing of the polar groups of adjacent chains. This might be anticipated from the fact that there are two "even" type units in the chain molecules to every one of the "odd" type. Strong meridian reflections must occur at the Bragg spacings corresponding to the approximate C–C component distance (1.25) along the fiber axis, but this is only observable with electron rays.[4]

We conclude from these results that a fiber pattern showing discrete reflections can be obtained from random copolymers composed of units which are able to crystallize together such as those comprising chain hydrocarbon spacers and small side polar groups. When equal numbers of units are present, the fiber period observed under such circumstances is given by the averages of those of the units present, but it bears no real relation to the structure present. There is evidence, however, that the longitudinal adjustment of adjacent chains is not random but is determined by the dipole interactions in such a way as to provide a minimum free energy for the entire structure. Recently Bunn and Peiser[5] reported a similar instance to that described here for a copolymer consisting of ethylene and hydroxyl substituted ethylene units. Bunn gives no information however about the kind of polar packing exhibited, so a full comparison with the results here reported is not possible.

Experimental

The polyesters were prepared by passing dry hydrogen through mixtures of the reactants at 200° until the degree of condensation was sufficient to allow fibers to be cold-drawn from solidified filaments. The dibasic acids all melted sharply and agreed with literature values for the respective compounds. The sebacic acid (m. p. 133°) was distilled from the commercial product. The 11- and 12-member acids (m. p.'s 110 and 124°) were prepared from 11-hydroxyundecylic acid and ω-bromoundecylic acid, respectively. From ultimate analysis the 11 member acid was estimated to be 97% pure. The ethylene glycol was redistilled from the C. P. laboratory product. About 5% excess of the equivalent amount of glycol needed for reaction was added and the mixture pre-condensed at about 120° until most of the water was removed. The condensation was then continued at 200° in bubbling hydrogen until the cold-drawing stage was reached.

The X-ray diagrams were taken on individual uniaxially oriented specimens. Filtered copper radiation was employed. Sodium chloride was dusted on the specimens as a reference standard. The fiber periods were calculated from the best reflections on several photographs. Five photographs were used to obtain the fiber period of the 14-membered polyester (16.84), four for the 15-

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(4) K. H. Storks, This Journal, **60**, 1753 (1938).

(5) Bunn and Peiser, *Nature*, **159**, 161 (1947).

member (36.32) and three for the 16-member (19.40). The fiber period of the copolyester (17.83) was taken from one sharp fiber pattern obtained at 6 cm.

Acknowledgment.—The author is indebted to B. S. Biggs, W. S. Bishop and R. H. Erickson for the preparation of the intermediates and the polyesters and to N. R. Pape for taking and measuring the photographs.

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RECEIVED JULY 31, 1947

Some Halogenated Naphthoxyacetic Acids[1]—A Confirmation

BY C. ROBERT GEISER AND HOKE S. GREENE

The preparation of 2,4-dichloro-1-naphthoxyacetic acid, 1,6-dibromo-2-naphthoxyacetic acid, 4-chloro-1-naphthoxyacetic acid, and 2,4-dibromo-1-naphthoxyacetic acid reported by Haskelberg[2] has been independently confirmed by us using similar methods. Templeman and Sexton[3] had previously reported the melting point of 2,4-dichloro-1-naphthoxyacetic acid as 135° but we have found it to be 178° in agreement with Haskelberg.[2]

The aforementioned compounds showed selectivity as weed killers in 0.1% solution as a triethanolamine salt. However, at that concentration they were not as effective as 2,4-dichlorophenoxyacetic acid.

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(1) From the M.S. thesis of C. Robert Geiser, University of Cincinnati, June, 1947.

(2) L. Haskelberg, *J. Org. Chem.*, **12**, 426 (1947).

(3) Templeton and Sexton, *Proc. Roy. Soc.* (*London*), **B133**, 300–313 (1946).

DEPARTMENT OF CHEMISTRY
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CINCINNATI, OHIO
RECEIVED JUNE 30, 1947

Separation of Tropic and Atropic Acids by Partition Chromatography

BY SIDNEY GOTTLIEB

In the course of a study on the hydrolysis of alkaloids of the atropine group, it became necessary to separate tropic from atropic acids in a large number of hydrolysates. Although the solubility characteristics of these two acids permit their separation from one another by several steps involving fractional crystallization, a much more rapid and convenient method was developed using partition chromatography.

This technique, originally developed by Martin and Synge,[1] consists essentially of passing one of a pair of immiscible solvents over a film of the other, the latter solvent being adsorbed onto an inert lattice. The substances dissolved in the mobile solvent will then partition themselves between the two phases according to their partition coefficients in such a way as to form distinct bands. Since tropic and atropic acids differ significantly in their partition coefficients between water and chloroform, this pair of solvents was used, with precipitated silicic acid as the supporting lattice. An acid–base indicator in the form of an azo dye was incorporated into the aqueous phase and, as the acids moved down the column, their positions were clearly indicated by dark blue bands against a red background.

In several parallel determinations, the identity of the first fraction to come through the column was established as atropic acid by evaporating the solvent and recrystallizing the residue once from hot water, which yielded monoclinic prisms, m. p. 106.0–106.5° (cor.). That the material comprising the upper band was tropic acid was proved by evaporating the solvent and recrystallizing the residue twice from boiling benzene to yield needes, m. p. 116.0–117.0° (cor.).

Experimental

A typical column was prepared by intimately mixing 10 cc. of a 0.1% aqueous solution of 3,6-disulfo-β-naphthaleneazo-N-phenyl-α-naphthylamine[2] with 20 g. of dry precipitated silicic acid. In this investigation Eimer and Amend C. P. silicic acid, batch #403320, was used. The mixing was done with a mortar and pestle until the mixture had uniformly taken on the red color of the dye, and no lumpiness remained. A slurry of this preparation was made with 50 cc. of chloroform and the slurry poured into a glass tube having a diameter of 24 mm., constricted and plugged with cotton at one end. When enough chloroform had run through the column so that the suspension acted like a stiff gel on shaking, a mixture of 5 mg. each of tropic and atropic acids dissolved in 3 cc. of chloroform was pipetted into the column. After this solution had just passed the top of the column, 5 cc. of chloroform was added to wash any acid remaining on the sides of the column into the narrow band. Then 50 cc. of chloroform was run through the column to separate and develop the bands. The atropic acid, being more soluble in chloroform, moved rapidly down in a sharp band, usually being completely washed out by 40 cc. of chloroform. The upper band, containing the slower-moving tropic acid, which had moved about one-fourth of the way down the column, was then washed through with a mixture of 10% ·butyl alcohol in chloroform. Titration of the residues with *N*/50 sodium hydroxide indicated essentially quantitative recovery and separation of the two acids.

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(1) Martin and Synge, *Biochem. J.*, **35**, 1358 (1941).

(2) Liddel and Rydon, *Biochem. J.*, **38**, 68 (1944).

CHEMICAL SECTION, MEDICAL DIVISION
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RECEIVED JULY 25, 1947

The Existence of Beta Cristobalite at Room Temperature

BY ALEXANDER GRENALL

Due to some unexplained circumstance, overheating of pelleted clay catalyst occurred in the regenerator kiln of a catalytic cracking unit to such a degree that some of the pellets were fused and glassy in appearance. On breaking open these pellets it was found that while the surfaces were glassy, the centers were not.

Independent X-ray diffraction examinations were made of the surface and center material. A complete analysis of the diffraction data from Debye–Scherrer photographs revealed, in addition to other phases, the presence of β-cristobalite in