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.

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BELL TELEPHONE LABORATORY
MURRAY HILL, NEW JERSEY
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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.

(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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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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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 the glassy surface of the pellets and the existence of α-cristobalite in the centers. The identity of these substances was established by comparison of the data from this work with that for β- and α-cristobalite given by the A.S.T.M. index,[1] excellent agreement in line position and relative intensities being shown.

Sosman,[2] in his authoritative treatise on silica, states that the inversion of the high temperature form, β-cristobalite, to the low temperature form, α-cristobalite, is rapid and occurs promptly as soon as the inversion temperature range of 200 to 275° is reached. In order to substantiate our identification of the β-cristobalite pattern for the overheated catalyst, a literature search was made and two other reported instances in which β-cristobalite had been identified in room temperature samples were found: in opals[3,4] and in glassy matrices containing silica.[4] In the latter publication this phenomenon was attributed to the prevention of inversion by the glassy matrix in which the crystals of β-cristobalite existed. Sosman[2,5] has denied the possibility of maintaining the beta structure by quenching but[5] has kept open the possibility that in a glass this might occur and asked for further study.

Our results are of interest because the cristobalite in the glassy surface of the fused clay catalyst pellets was shown to be the beta form while in the non-glassy interior, complete inversion to the alpha form had taken place. This provides an excellent confirmation of Greig's[4] contentions that the high-low inversion of cristobalite may be restrained and the high temperature form, β-cristobalite, may exist indefinitely at room temperature when the crystals of cristobalite are formed in a glassy medium. At the same time the results on the non-glassy centers are in agreement with Sosman's contention that the transformation to the alpha form cannot be delayed by quenching, if now this statement is qualified to apply to the changes occurring in a non-enclosing solid medium. As demonstrated by Greig,[4] when adhesion between enclosing medium and cristobalite crystal is broken, then inversion to the low temperature form takes place readily. Furthermore, from his results, it appears that once the α form has been developed, cristobalite may be taken up and down through the high-low inversion point with rapid transformation into the phase expected in complete accord with Sosman's statement.

It may be of significance to researchers in the field of ceramics to note that the diffraction patterns of both α- and β-cristobalite showed practically the same extent of line broadening. From the information that line broadening is present, it is possible to fix an upper limit to the crystal size of the cristobalites at 10^{-5} cm. Since the lines are only moderately broadened by comparison with sharp diffraction lines of the other phases present it is estimated that the crystal size lies between 5×10^{-6} and 10^{-5} cm.

THE UNION OIL COMPANY OF CALIFORNIA
WILMINGTON, CALIFORNIA
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[1] First Supplement to the card file of X-ray diffraction data published by the American Society for Testing Materials, 1944.

[2] R. B. Sosman, "Properties of Silica," A. C. S. Monograph Series 37, Reinhold Publishing Corp., New York, N. Y., 1927, p. 126.

[3] I. Levin and E. Ott, THIS JOURNAL, 54, 828 (1932).

[4] J. W. Greig, *ibid.*, 54, 2846 (1932).

[5] R. B. Sosman, *ibid.*, 54, 3015 (1932).

Crystallization of Triacetin

BY BERNARD HANCOCK, DONALD M. SYLVESTER AND SYLVAN E. FORMAN

Triacetin has been reported to form a glass at -78 and at $-60°$.[1] We have observed triacetin to crystallize at $+3.2°$.

A tank car of impure triacetin which had been shipped a long distance in cold weather was received with the contents partly solidified. Some of this slush was kept overnight in a refrigerator at $+5°$, but the solids had melted before morning.

The melt would not crystallize when cooled with dry ice or with an ice and salt mixture, but a portion diluted with an equal volume of absolute ethyl alcohol was crystallized readily by cooling to about -10 or $-15°$. Several such portions were crystallized on that day and some crystals were preserved in an ice and salt mixture.

On subsequent occasions, crystallizations of triacetin samples were induced by seeding. However, no crystals could be obtained without this aid.

A sample of triacetin was distilled at 130.5° (7 mm.). It had $n^{26}\mathrm{D}$ 1.4288 and gave saponification equivalents of 72.42 and 72.35 (theory 72.70). Five small portions were cooled to about $-15°$ and the first one was seeded with triacetin. This tube was used to seed the second tube, the second to seed the third, and so forth. This procedure was carried out to prevent impurities from being transferred by the seed crystals. Finally about 10 ml. of pure triacetin in a shielded tube was cooled to about $-15°$ and seeded from the fifth tube. The temperature rose to $+3.2°$ (cor.) where it remained until all of the solid melted.

The triacetin was converted into glycerol and ethyl acetate with ethyl alcohol and a trace of sulfuric acid. The glycerol was vacuum steam distilled. It was 98.5% glycerol by acetylation and 1.3% water by Karl Fischer titration; $n^{25}\mathrm{D}$ 1.4698.

The ethyl acetate was purified by extraction with water followed by rectification. It distilled at 77° and was 99.3% pure by saponification.

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[1] "Beilstein," Vol. II, first supplement, p. 70; second supplement, p. 161.

TECHNICAL DEVELOPMENT LABORATORY
U. S. INDUSTRIAL CHEMICALS, INC.
BALTIMORE, MARYLAND
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Alpha and Beta Schardinger Dextrin Nitrates

BY N. S. GRUENHUT, M. L. CUSHING AND G. V. CAESAR

French and Rundle[1] have accurately determined by X-ray diffraction and crystal density measurements the molecular weights of the α and β-Schardinger dextrins. The α-dextrin was shown to consist of six, and the β-dextrin of

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[1] French and Rundle, THIS JOURNAL, 64, 1651 (1942).