temperature rapidly rose to 170° with mild refluxing.[6] An additional 5 moles of pyridine was then added at such a rate as to maintain reflux, followed by heating the stirred mixture under reflux for 15 hr. It was then allowed to cool to about 100°, diluted with water, and worked up essentially by the method described by Crook,[2] except that benzene alone was used for the extraction instead of a benzene-ligroin mixture. Distillation through a 30-cm. Vigreux column yielded 762 g. (45%) of a mixture of 2- and 4-benzylpyridine at 150–160°/25 mm.

Oxidation. A solution of 348 g. of potassium permanganate in 1740 ml. of water was prepared at about 60°. To this was added with stirring 500 ml. of benzene containing 254 g. (1.5 moles) of the mixture of monobenzylpyridines obtained above. The mixture slowly rose to boiling and refluxed mildly for 3 hr. without external heating. Then the temperature dropped and the mixture was heated under reflux for 15 hr. Heating was discontinued and a solution of 30 ml. of conc. sulfuric acid in 60 ml. of water was added dropwise. Stirring was continued for 1 hr. Then the dense, finely divided manganese dioxide formed in the reaction was allowed to settle and the two phase benzene-water mixture was decanted, or siphoned off and separated. The water layer (mildly basic at this point) was discarded and the benzene layer saved for extraction as described below.

Separation of 2- and 4-benzoylpyridine.[7] A solution of 1600 ml. of 0.75*N* hydrochloric acid was prepared. The benzene solution obtained above was extracted with two 100-ml. portions of this acid solution and these acid extracts were discarded.[8] The benzene solution was then extracted four times with 350-ml. portions of acid and followed at the end with a 100-ml. water wash. The benzene layer was dried briefly over sodium sulfate and the benzene distilled leaving a residue of about 100 g. of 2-benzoylpyridine. Though somewhat discolored, this material was essentially pure, giving a picrate of m.p. 127–129°. Fractionation gave a quantitative recovery at 177–179°/15 mm., n_D^{23} 1.6070 (lit.[3d] b.p. 315–319°/750 mm.; picrate, m.p. 128–129°).

The four acid extracts and the water wash were combined and extracted three times with 150-ml. portions of benzene.[9] The aqueous phase was then heated on the steam bath to remove dissolved benzene, then cooled and rendered basic with sodium hydroxide while stirring. The crude 4-benzoylpyridine which crystallized amounted to 95 g. and had m.p. 60–65°. Recrystallization from a mixture of isopropyl alcohol and water yielded 70 g. (two crops) of material of m.p. 71–73° (lit.[3d] m.p. 72°).

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RESEARCH LABORATORIES
J. T. BAKER CHEMICAL COMPANY
PHILLIPSBURG, N. J.

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[6] When the theoretical amount of pyridine was present during this exothermic phase, the reaction usually became uncontrollable. The reaction was carried out on a scale several times that described here without difficulty when only half of the theoretical amount of pyridine was added initially, and the remainder after the temperature reached its peak.

[7] The authors have not investigated the use of countercurrent extraction for this separation. This modification would obviously simplify the process and make the separation more quantitative.

[8] These acid extracts contain about 25 g. of a mixture of unreacted monobenzylpyridines and 4-benzoylpyridine. This material can be recovered by the addition of sodium hydroxide and used on a later oxidation.

[9] These benzene extracts were found to contain a total of about 30 g. of material consisting mostly of 2-benzoylpyridine, but contaminated with some of the 4-isomer.

Separation and Identification of Aliphatic Mercaptans by Chromatography of the 2,4-Dinitrophenylsulfides

JOHN F. CARSON AND FRANCIS F. WONG

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This communication reports the separation of 2,4-dinitrophenylsulfides of some of the aliphatic mercaptans by adsorption chromatography on silicic acid containing fluorescent zinc sulfide. Although sensitive methods for the isolation and identification of mercaptans as the heavy metal mercaptides or as the dinitrophenylsulfides are well known, resolution of mixtures of the derivatives has not been reported except where fractional crystallization was employed.[1]

For chromatography, the general procedure of Sease[2] was employed except that celite was omitted. A commercial grade of silicic acid[3] was used without pretreatment and was mixed with one percent of its weight of fluorescent zinc sulfide.[4] The dinitrophenylsulfides were applied to the silicic acid–zinc sulfide columns in benzene solution and the adsorbed bands resolved by development with solutions of hexane containing acetone, ethyl acetate, or diethyl ether in ratios of 25–50:1. Illumination of the column in the dark with a mercury ultraviolet lamp revealed individual bands of dinitrophenylsulfides as grey to purple shadows on a yellow fluorescing background. Although the derivatives themselves are yellow to orange, detection of the zones in daylight is usually difficult and observation of the quenching of fluorescence is necessary for sharp definition. The rates of movement of alkyl dinitrophenylsulfides were found to increase in the order: $CH_3 < C_2H_5 < CH_2{=}CH{-}CH_2 < nC_3H_7 < nC_4H_9 < nC_5H_{11} < tC_4H_9 < nC_6H_{13}$. Mixtures of any of these derivatives could be resolved into separate distinct bands which could be isolated as pure compounds. However, mixtures of isomeric alkyl-2,4- dinitrophenylsulfides, with the exception of the *t*-butyl derivative, could not be resolved into separate distinct bands. For example, mixtures of isopropyl and *n*-propyl derivatives or of isobutyl- and *n*-butyl dinitrophenylsulfides moved as broad diffuse zones without splitting into separate bands. The rates of movement of the bands generally in-

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[1] C. Mannich and Ph. Fresenius [*Arch. der Pharm.*, 274, 461–72 (1936)] separated a mixture of *sec*-butyl- and propenyl 2,4-dinitrophenylsulfides by fractional crystallization.

[2] J. W. Sease, *J. Am. Chem. Soc.*, 69, 2242 (1947); 70, 3630 (1948).

[3] Mallinckrodt 100 mesh, Analytical Reagent. Mention of commercial products does not imply endorsement by the Department of Agriculture or recommendation over other products.

[4] No. 62 fluorescent zinc sulfide, Patterson Screen Division, E. I. du Pont de Nemours and Co., Inc., Towanda, Pa.

creased with developing solvent in the order: ether < ethyl acetate < acetone as expected, and hexane-ether solutions generally gave better separations as was observed by Sease.[2]

In the attempt to separate isomeric mercaptan derivatives, chromatography of the 2,4-dinitrophenyl alkylsulfones on silicic acid–zinc sulfide was attempted. The derivatives were more strongly adsorbed than the corresponding sulfides and moved as sharp bands when developed with hexane–acetone (25:1), but quenching of fluorescence was weaker. These derivatives possessed no apparent advantage over the sulfides and again mixtures of the isomeric derivatives could not be resolved into separate bands.

Chromatography of dinitrophenyl sulfides when combined with lithium aluminum hydride reduction[5] of disulfides has been found particularly useful for characterization of small quantities of unsymmetrical aliphatic disulfides. The 2,4-dinitrophenylsulfides can be prepared directly from the reduction mixture after destruction of excess lithium aluminum hydride. In some cases, a purer derivative may be obtained in this manner from the disulfide than from the mercaptan as we have observed with the derivative of allyl mercaptan. On the other hand, reduction with metals and acids is difficult with small quantities if isolation is necessary and is not applicable to allylic disulfides. Reductions with sodium in ether[1] or with sodium or sodium-potassium alloy in xylene[6] are time-consuming and, in our hands, have not been satisfactory for small quantities of diallyl disulfide.

Lithium aluminum hydride reduction, formation of dinitrophenylsulfides, and chromatographic separation of the derivatives has been applied to a 100-μl. sample of synthetic allyl propyl disulfide and to a 60-μl sample of methyl n propyl disulfide isolated by gas-liquid partition chromatography of volatile material from onions. In each case, the crystalline 2,4-dinitrophenylsulfides were obtained as pure compounds after chromatography.

EXPERIMENTAL

Materials. The saturated aliphatic mercaptans were of Eastman "White Label" Grade except for *iso*propyl- and *t*-butyl mercaptans which were Eastman Technical Grade. Before use, the purity of the mercaptans was usually established by gas-liquid chromatography on columns packed with a polyethylene glycol as the liquid phase. Allyl mercaptan was prepared by alkaline hydrolysis of allyl isothiourea hydrobromide and freshly prepared material was used in preparing the dinitrophenylsulfide. 2,4-dinitrophenylsulfides were prepared according to the procedure of Bost.[7] It was also found that these derivatives could be prepared conveniently from lead mercaptides by refluxing a suspension of lead mercaptide in ethanol containing an excess of 2,4-dinitrochlorobenzene or 2,4-dinitrofluorobenzene.

Preparation of chromatographic columns. Silicic acid[3] was mixed with 1% of its weight of fluorescent zinc sulfide[4] and the mixture shaken and tumbled for 5–10 min. The chromatograph tubes were packed with dry adsorbent with suction and the columns prewashed with one bed volume of anhydrous ether followed by two or three volumes of hexane. The dinitrophenylsulfides in benzene solution were added to the top of a column with a pipet and the column was again washed with two or three bed volumes of hexane before applying the developing solvents. For the separation of mixtures containing 1–5 mg. of derivative, a 11 × 200 mm. Pyrex glass tube was used, and for mixtures of dinitrophenylsulfides prepared from the reduction products of 50–100 mg. of disulfides a column 46 × 300 mm. was used.

Reduction of methyl-n-propyl disulfide and formation of 2,4-dinitrophenylsulfides. Sixty μl. of methyl *n*-propyl disulfide, previously identified by infrared spectra, was dissolved in 10 ml. of dry ether and placed in a 50-ml. round-bottom flask equipped with reflux condenser and a drying tube. Approximately 0.3 g. of lithium aluminum hydride (the quantity of reagent is not critical provided an excess is used) was added in small quantities over a 15-min. period. The mixture was refluxed gently for 2 hr. on a steam bath and then cooled in a Dry Ice bath. Excess lithium aluminum hydride was destroyed by the addition of 1 ml. of ethyl acetate followed a few minutes later by 1 ml. of water in 5 ml. of ethanol. After standing for 30 min. at room temperature, the mixture was poured into 50 ml. of ethanol containing 190 mg. of 2,4-dinitrochlorobenzene. The light amber suspension was warmed on the steam bath for 10–15 min., filtered from hydroxides and salts, and the gelatinous precipitate washed with 20 ml. of warm ethanol. The combined filtrates containing the dinitrophenylsulfides were concentrated *in vacuo* to a dry yellow solid which was extracted with 100 ml. of benzene. The benzene extract was washed with normal sodium hydroxide (to remove any dinitrophenol which interferes in chromatography), dried with calcium chloride, and concentrated *in vacuo* to 25 ml.

Chromatography of dinitrophenylsulfides. The benzene solution of dinitrophenylsulfides was poured on a column of silicic acid–zinc sulfide (1%), 46 × 200 mm., which had been prewashed with 120 ml. of ether and 400 ml. of hexane to give a yellow band, 0.5 cm. in thickness at the top. Washing with 400 ml. of hexane followed by development with 1750 ml. of hexane–ethyl acetate (25:1) resolved the band into an upper band (1 cm. wide) which had moved 3.5 cm. and a lower band (2.5 cm. wide) which had moved 13–14 cm. The slow-moving band was carved out of the column and extracted with acetone. Evaporation of the acetone and recrystallization of the yellow solid residue from 7 ml. of ethanol yielded 62 mg. of methyldinitrophenylsulfide as canary yellow micaceous plates identified by melting point, 120°, and mixed melting point. The faster moving band was eluted from the column with acetone. Removal of solvent yielded semi-crystalline material which was crystallized from 5 ml. of ethanol to yield 82.5 mg. of *n*-propyl dinitrophenylsulfide as stubby amber prisms, m.p. 84–85°.

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WESTERN REGIONAL RESEARCH LABORATORY
WESTERN UTILIZATION RESEARCH & DEVELOPMENT DIVISION
AGRICULTURAL RESEARCH SERVICE
U. S. DEPARTMENT OF AGRICULTURE
ALBANY, CALIF.

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