was not sufficient for adequate determination of physical properties. The infrared spectrum indicated slight contamination by alcohol; in other regions the spectrum was quite similar to that of 1-chloro-2-bromopropane except for a medium-intensity band at 9.05 μ not found in the latter. Since the product mixture from the addition reactions contained only very small amounts, if any, if 1-bromo-2-chloropropane, no further attempts to prepare this isomer were made.

Addition reactions. With acetic acid solvent. Solutions prepared in nitrogen-filled flasks from glacial acetic acid (50 g.), anhydrous hydrogen bromide (45 g., 0.56 mole), and allyl chloride (0.26 to 0.65 mole) were kept in cold rooms at 18°, 0°, or −18° (±1°) for 2 to 6 weeks. The shorter reaction times were generally used with the more concentrated solutions and usually led to recovery of more allyl chloride. Each solution was poured into 150 g. of ice water. The lower layer was separated, washed with dilute sodium carbonate and with water, dried, and distilled. After most of the allyl chloride had been removed, the infrared spectrum of the residual liquid was recorded. The product composition was estimated by comparing this spectrum with those obtained with pure samples and known mixtures of allyl chloride and the isomeric chloro bromides. In nearly all experiments, this estimation was confirmed by distillation of the residual liquid.

In 7 experiments (2 each at 18° and 0°, 3 at −18°), yields (based on unrecovered allyl chloride) of chlorobromopropanes were in the range 64–81%. The product mixtures were composed of 1-chloro-2-bromopropane (90 ± 2%) and 1-chloro-3-bromopropane (10 ± 2%). In 2 other experiments, the reaction flasks became unstoppered during the long period of standing and the product distributions were greatly altered (49% and 78% 1-chloro-3-bromopropane).

Without solvent. Anhydrous hydrogen bromide (122 g., 1.5 moles) was added during 5 hr. to allyl chloride (50 g., 0.65 mole) in an atmosphere of nitrogen. The solution was kept in a cold room for 2 to 3 weeks and was subsequently processed in the manner described for the experiments with solvent. In 4 experiments (2 each at −18° and 18°) the product mixtures, obtained in 65–71% yields, were composed of 1-chloro-2-bromopropane (91 ± 1%) and 1-chloro-3-bromopropane (9 ± 1%). In one experiment (at 0°) from which air was not excluded completely, the lower yield of product mixture was mainly 1-chloro-3-bromopropane (92%).

Attempted isomerizations of addition products. Solutions prepared by adding 10.0 g. (0.064 mole) of 1-chloro-2-bromopropane or of 1-chloro-3-bromopropane to a mixture of 10.0 g. (0.12 mole) of anhydrous hydrogen bromide and 10.0 g. of glacial acetic acid were kept at 18° for 6 days. The chloro bromides were recovered by dilution of the solutions with water. Washing, drying, and distillation led to recovery of 98–99% of the starting chlorobromopropane. No isomerization could be detected.

COATES CHEMICAL LABORATORIES
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LA.

Formylation of Thianaphthene with *N*-Methylformanilide

V. V. GHAISAS[1]

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The formation of thiophenecarboxaldehyde by direct formylation of the thiophene nucleus employing *N*-methylformanilide and phosphorus oxychloride was reported.[2] By modification of the procedure, Weston and Michaels[3] were able to obtain a 9% yield of a compound thought to be 3-thianaphthenecarboxaldehyde, when thianaphthene was allowed to react with *N*-methylformanilide in the presence of phosphorus oxychloride. Although the product melted at 58°, the same melting point as the 3-isomer, these investigators reported that it formed a phenylhydrazone melting at 204–205° On the other hand, Komppa and Weckman[4] reported the melting point of this derivative to be 115°.

The work has now been reinvestigated. Thianaphthene was formylated,[3] and a compound melting at 58° was obtained in 7% yield. However, the phenylhydrazone of this product melted at 115°, which agrees with the one reported in the literature.[4] The melting points of the oxime and the semicarbazone[5] also agreed with those of the 3-isomer to be found in the literature.

The 3-isomer was then obtained from 3-chloromethylthianaphthene by applying the Sommelet reaction.[2] The melting point of this product was not depressed by admixture with the one prepared by formylation of thianaphthene. The ultraviolet absorption spectrum of the compound obtained by formylation showed that it has a molecular extinction coefficient of 8526 at its maximum at 302 mμ. This, however, does not assist in differentiating between the two isomers.

EXPERIMENTAL

The absorption spectrum was taken on a Beckman quartz spectrophotometer using a 1.14×10^{-4} molar solution of the aldehyde in 95% ethanol.

RESULTS

The results give evidence that formylation of thianaphthene with *N*-methylformanilide gives 3-thianaphthenecarboxaldehyde.

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ORGANIC CHEMISTRY AND ENZYMOLOGY
FORDHAM UNIVERSITY
NEW YORK 58, N. Y.

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[1] Post-doctoral Fellow from the University of Bombay, India.

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