Anal. Calcd. for $C_{16}H_{34}O_6$: C, 59.59; H, 10.62; MR, 86.4. Found: C, 59.71; H, 10.94; MR, 85.4.

Acknowledgment. This work was sponsored by the Cities Service Research and Development Company in the form of a research fellowship.

DEPARTMENT OF CHEMISTRY
OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE
STILLWATER, OKLA.

The Addition of Hydrogen Bromide to Allyl Chloride[1]

JAMES G. TRAYNHAM AND JOHN S. CONTE

Received December 7, 1956

The ionic addition of hydrogen bromide to allyl chloride would appear to be a rather simple reaction, which should follow Markownikoff's rule. However, conflicting reports have appeared in the literature. Shostakovskii[2] reported an unusual dependence of orientation on temperature; the addition reaction yielded 1-chloro-2-bromopropane exclusively at 18°, 1-chloro-3-bromopropane at −19°, and equal amounts of the two isomers at 0°. That same year Antsus,[3] referring to Shostakovskii's work, claimed that the orientation is independent of temperature (−19° to 18°) and that in all cases he obtained only 1-chloro-2-bromopropane. Although the earlier paper has been quoted in a recent review,[4] Antsus' work appears to have been overlooked.

Because an actual temperature dependence such as was claimed[2] would be theoretically significant, we have reexamined the ionic addition of hydrogen bromide to allyl chloride with particular attention to olefin purification,[5] exclusion of air and light,[5] and possibilities of product isomerization. The procedures previously described[2,3] were followed closely. Products were identified by comparison of physical and spectral properties with those of authentic samples independently synthesized.

Contrary to both previous reports,[2,3] mixtures of isomers were obtained in all experiments. Except in those experiments in which we failed to exclude air completely, the product distribution was virtually invariable with Markownikoff orientation predominating (90 ± 2%). The orientation was independent of temperature (−18° to 18°), of the use of acetic acid solvent, and of reaction time. When air was admitted, the peroxide-effect[5] led to greatly altered product distributions. No isomerization could be detected when either of the two isomeric products (1-chloro-2-bromopropane and 1-chloro-3-bromopropane) was treated with hydrogen bromide under the same conditions used in the addition reactions. This observation precludes the possibility that either chlorobromopropane is an intermediate in the formation of the other. That is, they are formed independently in the reaction mixture, probably from two different intermediates or transition states.

Based on the report[6] that some migration of chlorine occurs in the addition of hypochlorous acid to Cl^{36}-labeled allyl chloride, an attempt was made to detect 1-bromo-2-chloropropane in the product mixture. Infrared spectral analysis[7] did indeed suggest the presence of very small amounts of this isomer mixed with the 1-chloro-2-bromopropane fraction, but conclusive evidence was not obtained.

EXPERIMENTAL[8]

Independent synthesis of the chlorobromopropanes. 1-Chloro-2-bromopropane and 1-chloro-3-bromopropane were prepared from phosphorus tribromide (0.27 mole) and the appropriate chloropropanol (0.53 mole). After the initial addition of phosphorus tribromide at 0°, the mixture was allowed to warm to room temperature and was stirred for 10 hr. longer. The 1-chloro-2-bromopropane[9] was obtained in 77% yield; b.p. 118–120°, n_D^{20} 1.4776, d_4^{20} 1.537. The 1-chloro-3-bromopropane[9] was obtained in 75% yield; b.p. 140–142°, n_D^{20} 1.4866, d_4^{20} 1.592. The infrared spectra of the two isomers were similar but were readily distinguished by the following non-common bands (s and m refer to strong- and medium-intensity absorption, respectively; numbers refer to wavelength in microns): for 1-chloro-2-bromopropane, 7.25 (s), 8.90 (m), 9.00 (m), 9.95 (s), 11.05 (s); for 1-chloro-3-bromopropane, 7.56 (s), 10.50 (s), 11.65 (s), 11.90 (s).

A small amount of 1-bromo-2-chloropropane[9b] was prepared in poor yield from thionyl chloride and 1-bromo-2-propanol (b.p. 67–70°/40 mm., n_D^{20} 1.4760, d_4^{20} 1.542; obtained in 62% yield by the reaction of 48% hydrobromic acid with propylene oxide[10]). In the one preparation attempted, the amount of 1-bromo-2-chloropropane obtained

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(1) From the M. S. thesis of J. S. Conte, Louisiana State University, August, 1956.

(2) M. F. Shostakovskii, *J. Applied Chem.* (*U. S. S. R.*), **9**, 681 (1936); *Chem. Abstr.*, **30**, 7538 (1936).

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(4) A. E. Remick, *Electronic Interpretations of Organic Chemistry*, 2nd ed., p. 446, John Wiley and Sons, Inc., New York, N. Y., 1949.

(5) To preclude free radical addition. M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933). F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).

(6) P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 3910, 3990 (1954).

(7) When one product mixture was distilled, several fractions boiling in a 1° range were collected. The infrared spectra of those boiling between 115° and 117° (very small amounts of material) showed medium-intensity absorption at 9.05 μ. This band gradually disappeared in the spectra of the fractions boiling between 118° and 122°. The independently prepared 1-bromo-2-chloropropane, alone of the three isomers, showed absorption at 9.05 μ.

(8) All infrared spectra were obtained with a Perkin-Elmer Model 21 double-beam recording infrared spectrophotometer (0.05 mm. cells, NaCl windows)

(9) (a) I. Heilbron, "Dictionary of Organic Compounds," p. 479, Oxford University Press, London, 1953 (b) A. Dewael, *Bull. soc. chim. Belges.*, **39**, 87 (1930).

(10) E. Abderhalden and E. Eichwald, *Ber.*, **51**, 1320 (1918).

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]

Received December 13, 1956

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.

Acknowledgments. This study was supported by grants of the National Science Foundation and the U. S. Public Health Service. The thianaphthene used was obtained through the courtesy of Dr. W. J. Coppoc of the Texas Company, Beacon, N. Y.

COMMUNICATION NO. 328 FROM THE DEPARTMENT OF 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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(5) Cagniant, *Bull. soc. chim. France*, 1949, p. 382.