[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Furan Reactions. VI. Cyclopropene

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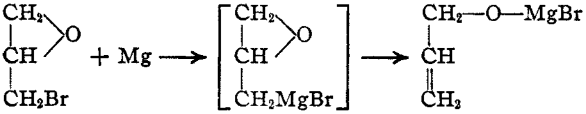
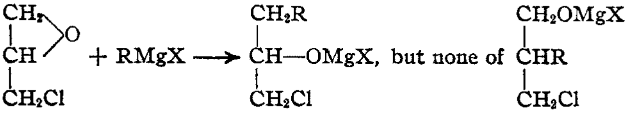
Cyclopropene has been prepared by Demjanov and Dojarenko[1] by pyrolyzing cyclopropyltrimethylammonium hydroxide. Its dibromide was stated to boil at 45° (27 mm.) and its tetrabromide at 155° (19 mm.). Cyclopropene was earlier mentioned by Freundler,[2] who reported having obtained it (as the bromide derivative) in the pyrolysis of barium furoate or calcium furoate. Freundler did not isolate cyclopropene as such. Cyclopropene was sought for in the products of electrolysis of sodium 1,2-cyclopropanedicarboxylate, but no evidence for it was observed.[3]

Freundler's method seemed attractive to study because of the availability of furoic acid. Accordingly, barium, calcium and sodium furoates were prepared and heated with or without soda lime under varying conditions (Freundler used soda lime). Furan and other products were formed but no appreciable yields of cyclopropene could be realized.

Two other reactions are of interest in this connection. The interaction of epibromohydrin with magnesium gave allyl alcohol



Cyclopropyl alcohol may have been in the reaction products but no definite evidence for it was obtainable. The reason for considering it as a possible reaction product is the analogy it bears to Koelsch and McElvain's[4] observation that Grignard reagents react with epichlorohydrin as follows



(A) (B)

In the present work, cyclopropyl alcohol is analogous to (A) and allyl alcohol is analogous to (B), if the —CH_2MgBr group reacts with the ethylene oxide ring of the same molecule.

β,β'-Dibromoisopropyl benzoate, $C_6H_5COOCH(CH_2Br)_2$, was synthesized from dibromohydrin and benzoyl chloride. This compound offers possibilities of change into cyclopropyl benzoate by reaction with zinc, but this was not investigated.

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(1) Demjanov and Dojarenko, *Ber.*, **55**, 2718 (1922); **56**, 2200 (1923).

(2) Freundler, *Compt. rend.*, **124**, 1157 (1897); *Bull. soc. chim.*, [3] **17**, 613 (1897).

(3) Fichter and Spiegelberg, *Helv. Chim. Acta*, **12**, 1152 (1929).

(4) Koelsch and McElvain, THIS JOURNAL, **51**, 3390 (1929); **52**, 1164 (1930).

Experimental Part

Barium Furoate.—Fifty grams of barium furoate was mixed with 15 g. of soda lime and put in an ordinary distilling flask which was connected in series to a water-cooled condenser, a receiver and a 2.5-liter gas-collecting bottle. The flask was heated by a moving flame, using a wire gauze, until gas evolution ceased. Then another identically charged distilling flask was substituted for the first one and the process repeated till 900 g. of barium furoate (equivalent to 860 g. of the anhydrous salt) had been dry-distilled. In all, 85 liters of gas was collected. In addition to an aqueous layer which was separated and discarded, about 130 g. of liquid was also collected.

Gas.—The gas was circulated through a coil condenser at −78° whereupon 35–40 cc. of liquid condensate was obtained. There was much uncondensed carbon monoxide. The condensate was fractionated, using a low-pitched, vacuum-jacketed spiral column.[5] Only 2 cc. of distillate appeared in the −30° range. The rest was almost entirely furan, 34 g. of which was collected. The 2 cc. of low boiling liquid was vaporized and analyzed by the absorption method.[6] Three-fifths of it dissolved in the acetylene reagent (alkaline K_2HgI_4), showing it to be methylacetylene. This was confirmed by isolating dipropinylmercury,[7] m. p. 202°, as a reaction product. The remaining two-fifths dissolved in 82% sulfuric acid (but not in 62%). Inasmuch as 82% sulfuric acid absorbs quantitatively all olefins which give rise to *sec*-alkyl hydrogen sulfates (such as propylene, α- or β-butylene, allene, butadiene, etc.) it may be assumed safely that cyclopropene would be absorbed also by this reagent. However, even if the absorbed portion were pure cyclopropene, which is extremely doubtful, its yield (which would be about 0.2%) is entirely unsatisfactory.

Liquid.—From the 130 g. of liquid, 90 g. of furan (b. p. 31–33°) was obtained, which made a total furan yield of 124 g. In addition, higher boiling liquids were present: (b. p., cc.) 40–50, 6; 50–100, 4; 100 (750)–95 (25 mm.), 7; 95–200 (25 mm.), 10 cc., which turned black as it entered the receiver. The last fraction may have contained difuryl ketone, as Freundler intimated. We did not press this point in view of Reichstein's recent work. Reichstein[8] was unable to isolate any pure difuryl ketone by this method but he did synthesize it in other ways (b. p. 150° at 12 mm.).

Non-production of Cyclopropene.—No better yields of cyclopropene were obtained when the heating was performed by a salt-bath at 345°, at which temperature a rapid gas evolution occurred. Also, nothing of interest in this connection was obtained when barium furoate was heated alone without the soda lime. This pyrolysis required careful watching to avoid too vigorous a reaction.

Since Freundler identified the cyclopropene as bromide derivatives, this was next carried out. Accordingly, the gas from 36 g. of barium furoate and 14 g. of soda lime when heated as before was collected over water and then passed[9] through a solution of bromine in chloroform at −10°. On fractionation, 0.5 cc. of a dibromide fraction (b. p. 32–40° at 17 mm.; n_D^{20} 1.5360) and 1 cc. of a tetrabromide fraction (b. p. 140–155° at 11 mm.; n_D^{21} 1.6192) were isolated. There is no certainty that these derivatives represent cyclopropene but the yield is very small in any event.

Other Salts.—A mixture of calcium furoate (36 g.) and soda lime behaved similarly, yielding about 5 liters of gas. This, in turn, gave rise to about 1 cc. each of dibromide and tetrabromide derivatives.

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(5) Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

(6) Hurd and Spence, THIS JOURNAL, **51**, 3356 (1929).

(7) Johnson and McEwen, *ibid.*, **48**, 469 (1926).

(8) Reichstein, *Helv. Chim. Acta*, **13**, 356 (1930).

(9) Trouble was usually encountered when the gas was passed directly into the bromine solution without previously collecting it.

Sodium furoate and soda lime gave more furan and less gas. The cyclopropene content of the gas, as determined by bromination, was small as in the previous cases.

Epibromohydrin.—This reagent was prepared from dibromohydrin using a method similar to that of "Organic Syntheses," Vol. III, for epichlorohydrin.

Two grams of epibromohydrin, 5 cc. of dry ether and 15 g. of turnings of magnesium-copper alloy (12.7% Cu) were placed in a flask. Action was started by a crystal of iodine. The spontaneous refluxing continued as a mixture of 78 g. more of epibromohydrin in 150 cc. of dry ether was added drop by drop. When all was added, it was refluxed for three hours on a water-bath. Then it was hydrolyzed and the ether layer distilled: b. p. 92–100°, 8 cc.; b. p. 60–65° (20 mm.), 6–8 cc.; b. p. 95–96° (15 mm.), 6–8 cc. None of these fractions showed any tendency to crystallize when left at −30° for forty minutes.

Allyl alcohol was confirmed in the 92–100° fraction by mixing 0.6 g. of it with 6 cc. of absolute pyridine and 2.8 g. of triphenylchloromethane. Thus there was formed allyl triphenylmethyl ether,[10] m. p. 74°. A mixed melting point with similar material made from known allyl alcohol was not depressed.

β,β'-Dibromoisopropyl Benzoate.—Forty-four grams of α,α'-dibromohydrin, $(BrCH_2)_2CHOH$, was mixed with 35 g. of benzoyl chloride and warmed until the evolution of hydrogen chloride ceased, usually less than half an hour. Then it was cooled, washed with sodium hydroxide, extracted with ether and distilled twice *in vacuo*. Forty grams of β,β'-dibromoisopropyl benzoate was collected at 185° and 16 mm. This is a 66% yield.

This ester did not solidify at −30° in three hours. Its density at 23.5° was 1.6324. The index of refraction values, n_D, were 1.5749 at 4.7° and 1.5658 at 24.8°.

Anal. Calcd. for $C_{10}H_{10}O_2Br_2$: Br, 49.8. Found: Br, 50.6.

Summary

Attempts to prepare cyclopropene by Freundler's method, namely, the dry distillation of a mixture of barium furoate or calcium furoate with soda lime gave negligible yields. Methylacetylene was identified as a reaction product but also in small amounts. Considerable furan was formed.

Allyl alcohol was produced as a result of the action of magnesium on epibromohydrin. β,β'-Dibromoisopropyl benzoate was synthesized.

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[10] Helferich, Speidel and Toeldte, *Ber.*, **56**, 766 (1923).