SPIROHEXANE

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In 1953 Slobodin and Blinova (1) reported an attempt to synthesize spirohexane by the treatment with zinc dust of 1,1-bis-(bromomethyl)-cyclobutane prepared from the corresponding diol and phosphorus tribromide. The only product isolated in the dehalogenation reaction was methylenecyclopentane. Rearrangement may have occurred in the dehalogenation step since similar rearrangements have been observed to occur as in the preparation of spiropentane (2). It is also possible that treatment of the diol leads to a rearranged dibromide since rearrangement has been noted in the treatment of cyclobutyl carbinol with phosphorus tribromide (3).

Spirohexane has now been prepared in good yield from 1,1-bis-(iodomethyl)-cyclobutane (I) and zinc in the presence of tetrasodium ethylenediaminetetraacetate to remove the zinc ions as formed in the reaction. This method was recently developed by Applequist *et al.* for the synthesis of spiropentane from pentaerythrityl tetrabromide (2). The 1,1-bis-(iodomethyl)-cyclobutane was prepared by the method of Schubert and Leahy (4) and its structure was checked by N.M.R., which showed two unresolved peaks with an area ratio of 2:3 at 104 and 260 p.p.10^8 from water due to the —CH_2I and cyclobutyl hydrogens, respectively. The spirohexane obtained by treatment of I with zinc dust showed no absorption in the infrared spectrum in the region for multiple bonds and had a N.M.R. spectrum which showed two peaks in an area ratio of 3:2 at 289 and 459 p.p.10^8 from water due to the cyclobutyl and cyclopropyl hydrogens, respectively (5).

Spirohexane has also recently been prepared by the reaction of methylenecyclobutane and methylene iodide in the presence of a zinc–copper couple (6).

EXPERIMENTAL

An "Aerograph" vapor chromatography unit fitted with a 10-ft Ucon Polar column was used with helium as the carrier gas. The N.M.R. spectra were determined on a 40-Mc/s Varian spectrophotometer with field stabilizer VK 3506, and methylene chloride was used as an external standard.

1,1-Bis-(iodomethyl)-cyclobutane (I)

1,1-Bis-(iodomethyl)-cyclobutane, b.p. 76–78° at 0.3 mm, was prepared in 50% yield by the method of Schubert and Leahy (4). A N.M.R. spectrum (0.5 ml/ml of carbon tetrachloride) showed two peaks at 104 and 260 p.p.10^8 from water with peak areas in the ratio of 2:3, respectively.

Spirohexane

In a 250-ml three-necked flask fitted with a reflux condenser, stirrer, and dropping funnel was placed 21 g of disodium dihydrogen ethylenediaminetetraacetate, a solution of 7.4 g of sodium hydroxide in 13 ml of water, 40 ml of 95% ethanol, and 0.6 g of sodium iodide. The mixture was heated to reflux and 5.5 g of zinc dust was added followed by 6.3 g of 1,1-bis-(iodomethyl)-cyclobutane which was added dropwise over a half-hour period. The mixture was refluxed an additional hour and distilled through a wire gauze column to give 2.8 g, b.p. 56–79°. Separation of the distillate by vapor chromatography gave 0.94 g (60%) of spirohexane, b.p. 70°, n_D^{22} 1.4245, D_4^{24} 0.855. Found: C, 87.65; H, 12.00%. Calc. for C_6H_{10}: C, 87.73, H, 12.27%.

Can. J. Chem. Vol. 38 (1960)

The infrared spectrum (liquid film) showed no bands in the region from 1500 to 2800 cm^{-1}. The N.M.R. spectrum (neat) showed two peaks at 289 and 459 p.p.10^8 from water with peak areas in the ratio of 3:2 respectively.

In addition to spirohexane the chromatogram of the crude product showed ethanol and an unidentified component for which the peak area was less than 3% of that for spirohexane.

Support for this research was received from the National Research Council of Canada and is gratefully acknowledged.

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Received May 27, 1960.
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AMINONITRILES. II. SOME DERIVATIVES OF 2-AMINO-3-CYANOINDENE*

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As part of a study on the relation between chemical structure and bacteriostatic activity, a series of 2-arylamino- (and aralkylamino)-3-cyanoindenes was prepared from the readily accessible 2-amino-3-cyanoindene.

The replacement of the unsubstituted amino group in β-iminonitriles (α-amino-β-cyanoethylenes) by anilino groups is normally accomplished (1, 2) by reacting the iminonitrile with the substituted aniline in acetic acid solution. This procedure was found to give variable results when applied to 2-amino-3-cyanoindene, and, in the case of 3-nitroaniline, 3-nitroacetanilide was isolated as the major product. Better results were obtained by heating the iminonitrile and the amine without solvent in the presence of the amine hydrochloride. The superiority of strong acid catalysis is to be expected in this type of nucleophilic addition to α,β-unsaturated systems (3). 2-(3,4-Dichlorobenzylamino)-3-cyanoindene was obtained in 95% yield by heating the iminonitrile and 3,4-dichlorobenzylamine with 5 mole% 3,4-dichlorobenzylamine hydrochloride. The 3,4-dichloroanilino derivative was prepared by simply fusing the iminonitrile with 3,4-dichloroaniline hydrochloride.

Although the action of concentrated sulphuric acid on 2-amino-3-cyanoindene gives 2-amino-3-carboxyindene in good yield (4), similar treatment of 2-(3,4-dichlorobenzylamino)-3-cyanoindene yielded the corresponding amide, 2-(3,4-dichlorobenzylamino)-indene-3-carboxamide, as the only identifiable product. The same amide was unexpectedly obtained when 2-amino-3-carboxyindene was heated with a mixture of 3,4-dichlorobenzylamine and its hydrochloride.

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*Report No. 26.