isolation (after 16 hr.) of formaldimedon (ethanol–water), m.p. 192–192.5°, pure or mixed with an authentic sample. The second peak (2.7 min.) was condensed in a small capillary and identified as methylpyrazine; infrared spectrum (carbon tetrachloride) identical with that of authentic material; picrate (ethyl acetate), m.p. 127°, softening at 128.5–130.5°, pure or mixed with an authentic sample of methylpyrazine picrate (m.p. 129–131°).

A third peak corresponding in retention time (4.1 min.) to vinylpyrazine built up gradually to about 1% yield at 380°. Collection of this substance did not afford enough material for derivative formation, but instantaneous decoloration of permanganate provided additional support for the assignment of vinylpyrazine to this peak.

Pyrolysis of 2-Pyridineethanol.[17]—Preheater was empty; column T, 190°; sample size, 6 μl. 2-Pyridineethanol was chromatographed essentially unchanged[18] at preheater T, 190° (infrared spectrum of eluate, retention time 11.2 min.). 2-Pyridineethanol was then chromatographed at preheater temperatures of 195, 230, 265, 285, 310, 340, 370, and 390° giving <1, ~ 1, 5, 10, 35, 55, 70, and 90% decomposition, respectively, to increasing amounts of two substances with retention times of 0.8 and 2.6 min. The first peak (0.8 min.) was identified as formaldehyde by conversion to formaldimedon (see preceding). Second peak (2.6 min.) was identified as 2-methylpyridine; infrared spectrum (chloroform); picrate (methanol), m.p. 165°, softening at 166–167°, pure or mixed with an authentics ample of 2-methylpyridine picrate. A third peak of retention time 4.0 min. built up gradually to about 1% yield at 370–390°. Two collections of this substance did not afford material for derivative formation. This material decolorized permanganate instantly and showed $\lambda_{\max}^{\text{EtOH}}$ 235 mμ,[19] thereby supporting the assignment of 2-vinylpyridine to this peak. A fourth broad peak, retention time 5.4–8.4 min., was present in the low-temperature runs but diminished in intensity at higher temperatures. Small samples were collected from 215° runs. This material decolorized permanganate instantly and showed $\lambda\lambda_{\max}^{\text{EtOH}}$ 235 and 277.5 mμ.[19] An infrared spectrum (very weak, cavity cell, chloroform) showed all of the major bands for 2-vinylpyridine.[20]

Pyrolysis of 4-Pyridineethanol.—Preheater was empty; column T, 190°; sample size, 6 μl. 4-Pyridineethanol was chromatographed at temperatures of 190, 240, 280, 320, and 355° giving over the entire range about 5% decomposition to a low, broad peak of retention time 6.8–13.6 min. At 355° there was only a small amount ($\sim 1\%$) of decomposition in the preheater to form peaks with retention times of 0.8, 1.0, 2.8, 3.2, 3.7, and 5.1 min. —a pattern which was qualitatively similar to that from a sample of phenethyl alcohol.[4] The main peak, retention time 18.4 min., was collected and identified as unchanged 4-pyridineethanol (infrared spectrum, chloroform). Material collected from the broad peak decolorized permanganate instantly and showed $\lambda_{\max}^{\text{EtOH}}$ 243 mμ. An infrared spectrum (weak, cavity cell, chloroform) showed all of the major bands for 4-vinylpyridine.

Pyrazineethanol and 2-pyridineethanol[21] can form strong intramolecular H-bonds. It is interesting to compare the retention times of pyrazineethanol (13.6 min.) and 2-pyridineethanol (11.2 min.) with that of 4-pyridineethanol (18.4 min.) which cannot form an intramolecular H-bond.[22]

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[17] In a preliminary run with a preheater packed with glass wool 2-pyridineethanol was chromatographed over a range of preheater temperatures. The decomposition was analogous to that from the corresponding series with pyrazineethanol: new peaks emerged at retention times corresponding to air, methylpyridine, and 2-vinylpyridine (estimated; no comparison with authentic material).

[18] Small peaks ($\sim 1\%$) at 4.0 and 5.8–8.4 min.

[19] Sample rinsed from collection capillary directly into cuvette. R. P. Mariella, L. F. A. Peterson, and R. C. Ferris, *J. Am. Chem. Soc.*, **70**, 1494 (1948), report for 2-vinylpyridine $\lambda_{\max}$ 235 mμ, log ϵ 4.1, and $\lambda_{\max}$ 278, mμ, log ϵ 3.7.

[20] Satdler curve #6654.

[21] P. R. Schleyer, C. Wintner, D. S. Trifan, and R. Bacskai, *Tetrahedron Letters*, **14**, 1 (1959), report for 2-pyridineethanol $\Delta\nu = 205$.

[22] C. H. DePuy and P. R. Story, *Tetrahedron Letters*, **6**, 20 (1959), report that internal H-bonding decreases retention time.

A Convenient Separation of *cis-* and *trans-*Methoxycyclohexanols

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A recent communication[2] regarding the separation of *cis-* and *trans-*cycloalkanediols by means of *n*-butylboronic acid prompts us to report some observations made about two years ago regarding the separation of the corresponding monoalkyl ethers by means of a lithium aluminum hydride–aluminum chloride reagent.[3] In attempts to equilibrate the epimeric 4-methoxycyclohexanols by this reagent (presumably[4,5] $AlHCl_2$) as previously described for the corresponding 4-methylcyclohexanols[6] we observed the immediate formation of a granular precipitate when ethereal solutions of the two alcohols were mixed with similar solutions of the hydride reagent. When the precipitate was collected, washed with ether, and then slurried with fresh ether and treated with 10% aqueous sulfuric acid, the 4-methoxycyclohexanol recovered from the ether layer was almost exclusively (>95%) the *cis* isomer as indicated by gas chromatographic analysis and preparation of the known[7] crystalline *p*-toluenesulfonate. In contrast, decomposition of the ethereal filtrate with 10% sulfuric acid led to *trans*-4-methoxycyclohexanol, identified by its crystalline hydrogen phthalate,[7] and shown, gas chromatographically, to be 87% isomerically pure.

Similar results were obtained with the 3-methoxycyclohexanols. Here, again, the precipitated material returned mainly *cis*-3-methoxycyclohexanol (90% pure by gas chromatography), identified by its hydrogen phthalate,[8] whereas the filtrate yielded the hitherto unknown *trans*-3-methoxycyclohexanol, characterized as its 3,5-dinitrobenzoate, in over 99% purity.

It was further observed that: (a) no separation occurred with the 2-methoxycyclohexanols (a precipitate formed but, upon decomposition, it yielded a mixture of isomers identical with the starting mixture); (b) the 4-methoxycyclohexanols yielded no precipitate with aluminum chloride alone and with lithium aluminum hydride alone they gave rise to a different precipitate which lead to little separation of isomers; (c) for obvious reasons, no precipitate formed from very *trans*-rich mixtures of 4-methoxycyclohexanol.

The previous observations may be explained readily if it is granted that the granular precipitates are intramolecular chelates as depicted in Fig. 1. Clearly such chelates can form only from the *cis*-4 and *cis*-3 isomers (not the corresponding *trans* forms), but presumably

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[1] The Radiation Laboratory is operated under contract with the U. S. Atomic Energy Commission. This note is taken in part from the Ph.D. dissertation of T. J. B.

[2] H. C. Brown and G. Zweifel, *J. Org. Chem.*, **27**, 4708 (1962).

[3] *Cf.* E. L. Eliel, *Rec. Chem. Progr.*, **22**, 129 (1961).

[4] E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 460 (1951).

[5] G. G. Evans, J. K. Kennedy, and F. P. Del Greco, *J. Inorg. Nucl. Chem.*, **4**, 40 (1957).

[6] E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960).

[7] D. S. Noyce, G. L. Woo, and B. R. Thomas, *J. Org. Chem.*, **25**, 260 (1960).

[8] D. S. Noyce, B. R. Thomas, and B. N. Bastian, *J. Am. Chem. Soc.*, **82**, 885 (1960).

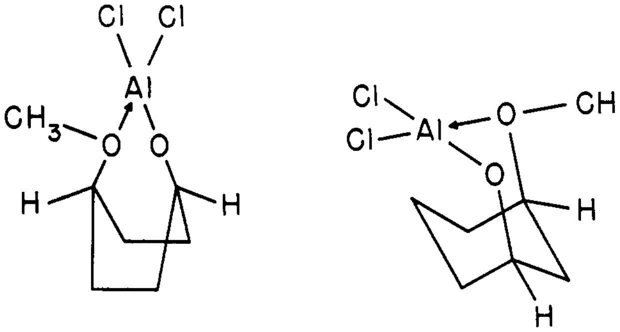

Figure 1

they might be formed from *both* isomers of 2-methoxycyclohexanol. Analysis of the chelates proved difficult (and is responsible for the delay in the publication of these results), for once formed the solids (which are quite hygroscopic) cannot be redissolved without decomposition. However, material was eventually obtained which was free of lithium (flame test) and which gave satisfactory analyses for C, H, and Al in the case of the 3-isomer and for Al and Cl in the case of the 4-isomer.[9]

Isolation of the species shown in Fig. 1 supports the hypothesis[3] that the active reagent formed from lithium aluminum hydride (1 mole) and aluminum chloride (>3 moles) is, in fact, $AlHCl_2$ and that the complexes formed from this reagent and substituted cyclohexanols which are subject to equilibration by ketones[6] are, in fact, of the composition $ROAlCl_2$.

The method here described probably lends itself to the separation of other epimeric pairs of alkoxycycloalkanols.

Experimental

4-Methoxycyclohexanol.—*cis*-Rich material was obtained by hydrogenating 124 g. (1.0 mole) of *p*-methoxyphenol in 300 ml. 95% ethanol at 130° and 2000 p.s.i. in the presence of 10 g. of Raney nickel. The theoretical amount of hydrogen was absorbed in 12 hr. The solution was filtered, concentrated, and partitioned between ether and water. The ether layer was washed, with 10% sodium hydroxide, followed by saturated aqueous sodium chloride, dried over magnesium sulfate, concentrated, and the residue distilled at 108–113° (24 mm.) to give 100.1 g. (77%) 4-methoxycyclohexanol. Gas chromatographic analysis on Tide (180°, He flow 24 ml./min.) indicated 61.6% *cis* isomer (retention time 13.7 min.) and 38.4% *trans* isomer (retention time 17.2 min.).

Chelate.—The mixed hydride reagent was prepared from 13.35 g. (0.10 mole) of aluminum chloride in 75 ml. of anhydrous ether and 0.025 mole of ethereal lithium aluminum hydride (*ca.* 1 *M*). To this solution was added with stirring 13.0 g. (0.10 mole) of the previous mixture of 4-methoxycyclohexanols in 50 ml. of anhydrous ether. The solution was stirred for 15 min., filtered in a dry atmosphere, and the precipitate was washed with four portions of anhydrous ether. It was dried in a desiccator at room temperature overnight for analysis.

Anal. Calcd. for $C_7H_{13}AlCl_2O_2$: Cl, 31.23; Al, 11.88. Found: Cl, 31.12; Al, 11.91.

In another run, the solid was stirred with ether and 10% aqueous sulfuric acid until two clear layers resulted. The ether layer was separated, washed successively with water, saturated sodium carbonate, and brine, dried over magnesium sulfate, and concentrated to give 4.09 g. (31.5% over-all or 51.1% of total *cis* isomer) of *cis*-4-methoxycyclohexanol of over 95% purity. The *p*-toluenesulfonate, formed in 75% yield, melted at 88–89.5° (lit.[7] m.p. 87.8–88.2°). Infrared spectrum of the alcohol was identical with one of pure *cis*-4-methoxycyclohexanol kindly provided by D. S. Noyce.

The ethereal filtrate by similar treatment yielded 3.90 g. (30% overall, or 78% of total *trans* isomer) of *trans*-4-methoxycyclohexanol of 87% purity, characterized by conversion to the hydrogen phthalate, m.p. 151–152° (lit.[7] m.p. 148.6–149.0) in 66% yield.

3-Methoxycyclohexanol.—Catalytic hydrogenation of 50.0 g. (0.40 mole) of *m*-methoxyphenol in 125 ml. 95% ethanol in the presence of 10 g. of 5% rhodium on alumina at 52 p.s.i. and room temperature was complete in 2.5 hr. The material was worked up as described for the 4-isomer to give 47.9 g. (92%) of 3-methoxycyclohexanol, b.p. 112–116° (28 mm.). Gas chromatographic analysis on a 5-ft. silicone QF-1 column at 155° and 40 ml./min. of helium indicated the product to contain 45.5% *trans* isomer (retention time 8.3 min.) and 54.5% *cis* isomer (retention time 11.0 min.). In a second hydrogenation, the product was 60% *trans* isomer.

Chelate.—To the mixed hydride solution prepared from 20.0 g. (0.15 mole) of aluminum chloride in 100 ml. of anhydrous ether and 0.0375 mole of ethereal lithium aluminum hydride was added 15.6 g. (0.12 mole) of 3-methoxycyclohexanol (60% *trans*) in 75 ml. of ether. The complex was collected after 30 hr. and weighed 10.3 g.; it was dried *in vacuo* at 56° for 16 hr.

Anal. Calcd. for $C_7H_{13}AlCl_2O_2$: C, 37.02; H, 5.77; Al, 11.88. Found: C, 36.76; H, 6.08; Al, 11.90.

In another run, starting with 28.6 g. (0.22 mole) of material containing 45.5% *trans* isomer, 0.20 mole of aluminum chloride in 100 ml. of ether and 0.05 mole of ethereal lithium aluminum hydride there was obtained 26.8 g. of solid complex which was decomposed as described for the 4-isomer and yielded 11.4 g. (39.5% over-all or 72.5% of total *cis* isomer) of *cis*-3-methoxycyclohexanol of 90% purity. This was characterized as the hydrogen phthalate, m.p. 103–104° (lit.[8] m.p. 104–105°), obtained in 51% yield.

Decomposition of the filtrate as described for the 4-isomer gave 9.85 g. (34.5% over-all or 76% of total *trans* isomer) of *trans*-3-methoxycyclohexanol of over 99% purity (gas chromatography), b.p. 105–106° (24 mm.), $n^{20}{}_{D}$ 1.4670. It was characterized as the 3,5-dinitrobenzoate, m.p. 104–105°.

Anal. Calcd. for $C_{14}H_{16}N_2O_7$: C, 51.85; H, 4.97. Found: C, 52.16; H, 5.28.

2-Methoxycyclohexanol.—Catalytic hydrogenation of guaiacol over rhodium on alumina (as described for 3-methoxycyclohexanol) yielded 2-methoxycyclohexanol, b.p. 66–67° (16 mm.), which was quite impure and required purification by preparative gas chromatography. The material collected was 90.3% *cis* and 9.7% *trans*. The pure *trans* isomer, b.p. 91.5–93.0° (24 mm.), $n^{20}{}_{D}$ 1.4595 (lit.[10] b.p. 72.5–73.2° (10 mm.), $n^{25}{}_{D}$ 1.4586), was obtained from cyclohexene oxide and methanol as previously described.[10] A mixture of the two preparations (5.20 g.) containing 52.3% *trans* alcohol was converted to the solid chelate in the manner described earlier. The alcohol recovered from the chelate (4.15 g.) contained 53.1% *trans* isomer whereas that recovered from the filtrate (0.58 g.) contained 73.1% *trans* isomer.

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[9] Inner complexes of aluminum similar to those shown in Fig. 1 have been described previously by G. Bähr and G. E. Müller, *Chem. Ber.*, **88**, 251 (1955).

[10] S. Winstein and R. B. Henderson, *J. Am. Chem. Soc.*, **65**, 2196 (1943).

Dibutyl 2-Bromoethaneboronate[1]

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Radical-catalyzed additions to dibutyl ethyleneboronate have made a variety of new types of carbon-functional organoboron compounds available.[2] Extension

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[2] D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).