from those originally found by us were obtained. With the 4-methyl material, excellent agreement with the recently reported result of Eliel and Ro[5] was obtained. With the 2-methyl material, agreement with the value reported by Hückel[4] last year was obtained and these two values were lower in *trans* content than other reports. Thus, these results with VPC clearly demonstrate that high values of the percentage of the isomer with the lower density were obtained in our earlier work.

It is of interest to look at the present results in terms of the concepts of "product development control" and "steric approach control" in the lithium aluminum hydride reduction.[2] In the case of the 3- and 4-methylcyclohexanols, the amount of stable isomer formed in the reduction is in excess of that found in the equilibrium mixture. As has been pointed out,[2] the relative contributions of the axial and the equatorial approaches in the case of the unhindered ketone (product development control) will depend upon the different energies of the two transition states involved. Since the relative energetics of the two aluminum coordinated species are not known, the equilibrium composition of the alcohols, themselves, serves as a first approximation of the energy difference. However, as already pointed out by Eliel and Ro,[5] in these two cases, this approximation must be on the low side as far as the stable isomer is concerned since any increase in bulk of the oxygen function will serve to increase the amount of the more stable isomer. Thus, the results obtained are in line with expectations derivable from this simplified concept. With regard to the composition of the 2-methylcyclohexanols obtained upon reduction, the presence of more of the less stable isomer than is found in the equilibrium mixture is to be expected on the basis of concurrent functioning of both steric approach control and product development control.

EXPERIMENTAL

The reductions were performed as described earlier.[2] The equilibrations also were conducted as previously[2] and approached from each side of the equilibrium mixture. The analyses were performed using an Aerograph Master A-100 Apparatus (Wilkens Instrument and Research, Inc., Walnut Creek, Calif.), equipped with a 10-inch column of 30% glycerol on Chromosorb.[6] The separations were performed at a temperature of 80 ± 5° with a helium flow rate of 90 ± 10 ml./min. Percentage compositions were obtained from planimeter-determined areas under the separate peaks and the values were reproducible to 1%. Retention times quoted below are taken from the time of injection of sample.

2-Methylcyclohexanols. At 88° and 90 ml./min. flow rate, the retention time for the *cis* isomer was 8.0 min. and for the *trans*-isomer was 15.4 min. The retention time for starting ketone at 80° and 100 ml./min. flow rate was 4.5 min.

3-Methylcyclohexanols. At 81° and 92 ml./min. flow rate, the retention times were 14.0 min. for the *trans* and 20.2 min. for the *cis*. Under ketone conditions, the starting material had an 8 min. retention time.

4-Methylcyclohexanols. Under the conditions used for the 3-methyl isomer, the retention time for the *cis* isomer was 14.6 min. and for the *trans* isomer was 21.3 min.

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(5) E. E. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5992 (1957).

(6) The use of glycerol columns for separation of isomeric cyclohexanols was reported by R. Komers, K. Kochloefl, and V. Bazant, *Chem. & Ind. (London)*, 1405 (1958).

5-Amino-3-chloropyridazine[1]

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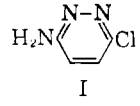
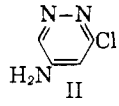
3,6-Dichloropyridazine undergoes reaction with ammonia to produce I, 6-amino-3-chloropyridazine (m.p. 213–214° dec.), as is well known.[3,4] It was of interest to determine whether the same compound resulted when sodium amide was caused to act on the dichloro compound. Rearrangements have frequently occurred when sodium amide has been used (*cf.*, *inter alia*, refs. 5,6). The aminochloro compound which was obtained in 64% yield melted at 141.5–142°, and was clearly not I. This has been assigned the structure of the rearrangement product, II, *viz.*, 5-amino-3-chloropyridazine. Present circumstances have precluded dehalogenation of II to 4-aminopyridazine, which was prepared by Kuraishi[7] subsequent to the completion of this work.



I



II

EXPERIMENTAL

A vigorously stirred solution of 14.9 g. (0.1 mole) of 3,6-dichloropyridazine in 150 ml. of xylene was treated with 12.0 g. (0.3 mole) of sodium amide and refluxed for 10 hr. To the brown mixture there was added an excess of aqueous hydrochloric acid. The layers were filtered and separated. The organic layer was extracted further with 6*N* hydrochloric acid, and the acidic extracts were concentrated prior to basification. A light tan solid (9.5 g., m.p. 135–138°) was obtained; four crystallizations from benzene-hexane mixture

(1) Pyridazines IV. Previous contribution: E. A. Steck, R. P. Brundage, and L. T. Fletcher, *J. Am. Chem. Soc.*, **76**, 4454 (1954).

(2) Present address: McNeil Laboratories, Philadelphia, Pa.

(3) E. A. Steck, R. P. Brundage, and L. T. Fletcher, *J. Am. Chem. Soc.*, **76**, 3225 (1954).

(4) J. Druey, Kd. Meier, and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

(5) R. Levine and W. C. Fernelius, *Chem. Revs.*, **54**, 483 (1954).

(6) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith, and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

(7) T. Kuraishi, *Pharmaceutical Bulletin (Japan)*, **4**, 137 (1956).

gave 8.3 g. (64% yield) of jagged blades, m.p. 141.5–142°. This was assigned structure II as 5-amino-3-chloropyridazine on the basis that it caused marked depression of the melting point of I when admixed with it, and that sodium amide is known to cause rearrangements.

Anal. Calcd. for $C_4H_4ClN_3$: C, 37.08; H, 3.11; Cl, 27.57. Found: C, 37.40; H, 3.13; Cl, 27.51.

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Synthesis of Mercaptophenols and Alkyl Derivatives

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We were interested in studying the behavior of mercaptophenols, containing both phenolic and aromatic mercaptan groups, in free radical processes. The use of a number of thiohydroquinones as polymerization inhibitors has been described by us in a recent patent.[1] A review of the literature indicated relatively few mercaptophenols having a thiocatechol or thiohydroquinone configuration have been described.[2–6] These compounds were usually prepared by reduction of the corresponding sulfonyl chloride.

A synthetic procedure is described in this report based on sulfurization of a phenol with sulfur monochloride. The crude sulfurization product, containing a mixture of monosulfide, disulfide, and polysulfide, is subjected to pressure hydrogenation using supported MoS_2 as a catalyst. The disulfides and polysulfides are reduced to the corresponding thiol.

A study was made of the sulfurization reaction using 2,6-xylenol as a prototype, aimed at maximizing the yield of thiol. The preferred sulfurization procedure was applied to phenol. Thiohydroquinone was recovered. Since thiocatechol was not detected, it was assumed that sulfurization occurred exclusively in the para position. The thiol derived from *o*-cresol was assigned a thiohydroquinone structure. The thiols of 2,4-xylenol, 4-*t*-butyl-*o*-cresol, 6-*t*-butyl-*o*-cresol, 2-*t*-butyl-*p*-cresol, 2-*t*-amylphenol, 2,6-diisopropylphenol, and 2,6-di-*t*-butylphenol were produced by the sulfurization-hydrogenation procedure. All the resulting mercaptophenols except the mercaptans derived from phenol and 2,6-xylenol are new compounds.

(1) U. S. Patent **2,810,765**, M. B. Neuworth and E. B. Hotelling, October 22, 1957.

(2) R. Leuckart, *J. prakt. Chem.*, (2), **41**, 179 (1870).

(3) G. Schwarzenbach and H. Egli, *Helv. Chim. Acta*, **17**, 1176 (1934).

(4) T. Zincke and K. Arnold, *Ber.*, **50**, 116 (1917).

(5) P. Karrer and P. Leiser, *Helv. Chim. Acta*, **27**, 678 (1934).

(6) E. Katscher and H. Lehr, *Monatsh.*, **64**, 236 (1934).

EXPERIMENTAL

Starting materials. 2,6-Xylenol and 2,4-xylenol were purchased from Reilly Tar and Chemical Co. Both materials were redistilled and shown to be pure by infrared analysis. 2-*t*-Amylphenol was obtained from Sharples Chemicals, Inc., and used without further purification. 2,6-Diisopropylphenol and 2,6-di-*t*-butylphenol were purchased from Aldrich Chemical Co., and used without further purification.

6-*t*-Butyl-*o*-cresol and 4-*t*-butyl-*o*-cresol were synthesized by sulfuric acid–catalyzed butylation of *o*-cresol with isobutylene. 6-*t*-Butyl-*o*-cresol was obtained by fractionation of the crude butylation mixture, boiling point 118° (20 mm.). 4-*t*-Butyl-*o*-cresol, the higher boiling isomer, was similarly recovered, boiling point 132° (20 mm.). 2-*t*-Butyl-*p*-cresol was formed by sulfuric acid–catalyzed butylation of excess *p*-cresol with isobutylene. The desired product distilled at 125–126° (20 mm.) and had a melting point of 51°.

Sulfurization-hydrogenation procedure. The preferred sulfurization-hydrogenation procedure was carried out as follows:

The apparatus consisted of a 1-l., 4-neck round-bottom flask equipped with heating mantle, stirrer, thermometer well, gas inlet tube, and dropping funnel with pressure equalizer, a reflux condenser and drying tube. One mole of 2,6-xylenol was dissolved in 500 ml. of carbon tetrachloride, containing 1 g. of sulfur. Dry nitrogen gas was bubbled slowly through the apparatus. Seventy-four g. (0.55 mole, 10% excess) of sulfur monochloride (Matheson technical) is dissolved in 200 ml. of carbon tetrachloride. Toluene may be used as the solvent instead of carbon tetrachloride with no loss in yield. The sulfur monochloride solution is added slowly through the dropping funnel with continued efficient stirring and nitrogen sweeping, and at such a rate that the reaction temperature does not exceed 30°. This addition generally requires 1 hr. When it is complete the solution is heated to reflux, held at this temperature for 30 min., and then allowed to cool to room temperature with continued stirring and nitrogen sweeping.

The crude disulfide is freed of solvent by distillation under low vacuum to a pot temperature of 120°/50 mm. (A water aspirator is the only practical source of vacuum, due to the exceedingly corrosive nature of the vapors.) The dark viscous residue is dissolved in toluene while still hot. It is then charged into a hydrogenation bomb constructed of Type 316 stainless steel, treated with 10% by weight of molybdenum disulfide (supported on alumina pellets; Davison Catalyst TS-55-3668), and hydrogenated at 140° (cold hydrogen pressure 1800 p.s.i.) until no further gas uptake is observed.

The hydrogenation product, after cooling to room temperature, is filtered to remove catalyst. The filtrate is distilled on a $^3/_4 \times 24$ in. Vigreaux column; approximately 15% of the 2,6-xylenol is recovered. The yield of 4-mercapto-2,6-xylenol, based on xylenol consumed, is 49%; it is accompanied by a 5% yield of 4-chloro-2,6-xylenol. The remainder of the product is high-boiling yellow oil, presumably mostly 4,4′-thiobis-(2,6-xylenol), plus an intractable tarry residue.

Discussion of results. The preferred sulfurization conditions were applied to phenol followed by hydrogenation of the crude sulfurization mixture. Thiohydroquinone,[7] a solid, melting point 32–35°, was recovered in 19% yield. The lower boiling analog, thiocatechol, could not be detected, indicating sulfurization occurs exclusively in the para position. Sulfurization-hydrogenation of *o*-cresol yielded a crystalline thiol,[8] m.p. 39–42°, in 28% yield. This com-

(7) Boiling point 149–150° (25 mm.). *Anal.* Calcd. for C_6H_6OS: C, 57.11; H, 4.79; S, 25.41. Found: C, 56.90; H, 4.95; S, 24.95. Ref. (4) reports the synthesis of thiohydroquinone, m.p. 29–30°, b.p. 144–146° (20 mm.).

(8) Calcd. for C_7H_8OS: C, 59.98; H, 5.75; S, 22.87. Found: C, 59.65; H, 5.75; S, 23.22.