and recrystallized from isoöctane to yield needles, m.p. 97–98°.

Anal. Calcd. for $C_{17}H_{19}O_3N$: C, 71.56; H, 6.71. Found: C, 71.41; H, 6.59.

Spectral Characteristics of α-Dolabrinol.—Electronic absorption (isoöctane): λ_{max} 248.5 (log ε 4.31), 325 (log ε 3.68), 356 (log ε 3.60), 365 (log ε 3.69), 374 (log ε 3.79).

Infrared absorption (KBr pellets): 3250s, 2970w, 2930w, 1637w, 1613w, 1585m, 1540s, 1520s, 1455s, 1420s, 1375s, 1305s, 1285s, 1265s, 1240s, 1195s, 1100w, 1060m, 1040w, 1013w, 962m, 908m, 895m, 815m, 795m.

N.m.r. (shifts in p.p.m. relative to tetramethylsilane as +10.0; carbon tetrachloride solution): +7.8 (CH_3O; relative intensity 3.0); +5.0, +4.8 (CH_2=; rel. int. at doublet 2.0); +3.0 (H—aromatic; rel. int. 3.0); +1.15 (OH; rel. int. 2.0).

Hydrogenation of α-Dolabrinol.—Quantitative hydrogenation in acetic acid, with palladium on charcoal as catalyst, using the analytical sample of α-dolabrinol dicyclohexylamine salt, resulted in an absorption equivalent to 348 mg. of substance per mmole of hydrogen (*vs.* calculated 359 mg.).

In another experiment, 51.0 mg. of α-dolabrinol was hydrogenated in 4 ml. of 95% ethanol in presence of 12 mg. of 5% palladium on charcoal. The absorption of hydrogen stopped after 15 min. stirring. Filtration, evaporation to dryness, and evaporative distillation of the residue at 2 mm. pressure gave 44 mg. of α-thujaplicinol (85% yield). The material obtained, run as a smear, and its benzylamine salt run as potassium bromide pellets, showed infrared spectra identical with those of the authentic α-thujaplicinol and its salt. The dicyclohexylamine salt melted at 128–129° and the benzylamine salt 113.0–114.0°; these melting points were not depressed by admixture with authentic samples. Previously[3] the melting point of the benzylamine salt was reported as slightly lower. The higher melting point reported here was also reproduced with chromatographically purified α-thujaplicinol benzylamine salt. Insufficient separation of α-thujaplicinol from α-dolabrinol in previous experiments probably accounts for the discrepancy.

Isolation of Isopygmaein.—A 1.9-g. portion of the *n*-hexane-soluble part of the *Papuacedrus torricellensis* extract[1] was chromatographed on S & S 470 paper impregnated with 21% phosphoric acid, using toluene as eluent, as described above. The material separated into two fractions, and the fraction with lower R_f was eluted with chloroform. The evaporation residue of eluate was taken up in 15 ml. of warm isoöctane, treated with small amounts of charcoal, filtered, and cooled to −5°. The separated crystals after recrystallization weighed 22 mg. and melted at 111.0–112.0°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; mol. wt. (Rast), 194. Found: C, 68.15; H, 7.49; mol. wt., 206.

The material was characterized further as copper complex (2:1), m.p. 272.5–273°.[12]

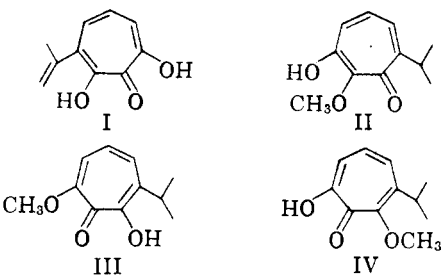
Anal. Calcd. for $C_{22}H_{26}O_6Cu$: C, 58.72; H, 5.82. Found: C, 58.52; H, 5.75.

Spectral Characteristics of Isopygmaein.—Electronic absorption (isoöctane): λ_{max} 373 (log ε 3.77), 358 (log ε 3.75), 326 (log ε 3.75), 313 infl. (log. ε 3.63), 250 (log ε 4.47).

Infrared absorption (KBr): 3220s, 2980m, 2890m, 1590m, 1555s, 1495m, 1475s, 1463s, 1445m, 1410s, 1390m, 1365m, 1337s, 1290s, 1243s, 1230s, 1210s, 1195m, 1168s, 1140s, 1095s, 1065m, 1035m, 990m, 920m, 855m, 800m, 783w, 760m, 675m. In carbon tetrachloride (0.23 *M*), the hydroxyl stretching peak shifted to 3060 cm.$^{-1}$ with decrease in intensity; neither intensity nor position was changed by dilution to 0.028 *M* solution. The carbonyl peak was found at 1602 cm.$^{-1}$.

The shift in position of the hydroxyl band upon dissolution was also observed for pygmaein. This was noted with other tropolones by Kuratani, *et al.*, and was explained by the existence of ring dimers with intermolecular hydrogen bonds in solid.[13]

Synthesis of Isopygmaein.—To a 595-mg. portion of α-thujaplicinol, $n^{25}D$ 1.6267, dissolved in 5 ml. of ethyl ether a solution of 150 mg. of diazomethane in 12 ml. of ethyl ether was added dropwise under stirring. The reaction was completed in a few minutes. The resulting mixture was evaporated to dryness, taken up in 20 ml. of warm isoöctane, treated with charcoal, filtered, and cooled to −5°. The separated crystals were filtered to give 138 mg. of material, m.p. 108–111° (28% yield); recrystallization raised the melting point to 110–111.5°. The substance obtained and its copper complex did not depress the melting point of the natural isopygmaein or its copper complex. Their infrared spectra and paper chromatograms were identical.



(12) At room temperature the copper complex of isopygmaein separated invariably in the form of gel-like voluminous material, either from alcohol or from isoöctane–chloroform mixture. The above crystalline modification was obtained by dissolving the material in hot isoöctane–chloroform mixture and removing the chloroform slowly on a steam bath.

(13) K. Kuratani, M. Tsuboi, and T. Shimanouchi, *Bull. Chem. Soc. Japan*, **25**, 250 (1952).

(14) (a) T. Nozoe, Y. Kitahara, and K. Doi, *Proc. Japan Acad.*, **27**, 282 (1951). (b) T. Nozoe, Y. Kitahara, K. Yamane, and T. Ikemi, *ibid.*, **27**, 193 (1951). (c) T. Nozoe, Y. Kitahara, E. Kunioka, and K. Doi, *ibid.*, **26**, (9) 38 (1950). (d) T. Nozoe and E. Sebe, *ibid.*, **26**, (9) 45 (1950).

Hydrogenolyses of Chloromethanes with Triphenyltin Hydride

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As part of a continuing study of the hydrogenolyses of organic halides with triphenyltin hydride, we are reporting on the stepwise hydrogenolyses of the chloromethanes.

When triphenyltin hydride was mixed with carbon tetrachloride at room temperature, an exothermic reaction took place which heated the solution to boiling. Chloroform was identified as one of the products by vapor phase chromatography, as well as by its n.m.r. spectrum. The companion product of the reaction, triphenyltin chloride, was identified by mixed melting point with an authentic

(1) Taken from a portion of the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, 1963.

(2) To whom inquiries should be sent.

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sample. The reaction was shown to be quantitative by titration of the triphenyltin chloride formed with standard alkali. No evidence for any other halogen containing product was found.

Chloroform reacted more slowly. After twenty-four hours at 30° only about 20% hydrogenolysis had occurred. Methylene chloride was identified as one product by vapor phase chromatography, the other product being triphenyltin chloride. At reflux for eighteen hours the reduction was nearly quantitative.

The reaction of triphenyltin hydride with methylene chloride at room temperature for thirty hours gave triphenyltin chloride in only 2% yield. However, when the reaction mixture was heated at reflux for eighteen hours, a 92% yield of triphenyltin chloride was found. Methyl chloride was identified as the other product by vapor phase chromatography and by its infrared spectrum.

In summary, the hydrogenolysis of the halomethanes is increasingly facile in the order: methylene chloride < chloroform < carbon tetrachloride. It is also noteworthy that the reactivity of the chloromethanes to reduction by triphenyltin hydride is the reverse of their apparent reactivities toward lithium aluminum hydride.[4] There is a reasonable possibility that this synthetic method using a triaryltindeuteride might offer a convenient method of selectively introducing deuterium into a poly-halogen containing molecule.

Experimental

Triphenyltin Hydride and Carbon Tetrachloride.—Upon mixing 1.383 g. (9.00 mmoles) of carbon tetrachloride and 0.702 g. (2.00 mmoles) of triphenyltin hydride, an immediate reaction took place with generation of heat. The reaction mixture was allowed to cool to room temperature (15 min.) and then dissolved in 100 ml. of a 1:1 mixture of benzene–ethanol. Titration with 0.2000 *N* sodium hydroxide to a Thymol Blue end point required 10.00 ml. (100%).

In a separate experiment, 1.053 g. (3.00 mmoles) of triphenyltin hydride was mixed with 1.400 g. (9.09 mmoles) of carbon tetrachloride in a constant temperature bath at 30° and allowed to stand for 24 hr. The vapor phase chromatograph showed two peaks attributed to carbon tetrachloride and chloroform by comparison with known compounds. The n.m.r. spectrum showed a band at 2.96 τ which increased in intensity when chloroform was added to the reaction mixture and the n.m.r. was rerun.

Triphenyltin Hydride and Chloroform.—A solution of 1.076 g. (3.64 mmoles) of triphenyltin hydride and 1.071 g. (9.00 mmoles) of chloroform was allowed to stand at 30° for 24 hr. Titration with 0.2000 *N* sodium hydroxide as above required 4.16 ml. (22%).

When a solution of 0.702 g. (2.00 mmoles)triphenylt in hydride and 1.066 g. (8.90 mmoles) of chloroform was heated under reflux at 70° for 13 hr., the titration required 9.89 ml. (98.7%).

In a second experiment, 0.554 g. (1.58 mmoles) of triphenyltin hydride was mixed with 0.955 g. (8.00 mmoles) of chloroform and allowed to stand 24 hr. at room temperature. The vapor phase chromatograph showed two peaks attributed to chloroform and to methylene chloride as shown by comparison with standards.

(4) V. H. Dibeler, *J. Research Natl. Bur. Standards*, **44**, 363 (1950).

Triphenyltin Hydride and Methylene Chloride.—A solution of 1.047 g. (2.98 mmoles) of triphenyltin hydride and 0.784 g. (9.22 mmoles) of methylene chloride was allowed to stand at 30° for 24 hr. Titration of the reaction mixture, as above, required 0.24 ml. of 0.2000 *N* sodium hydroxide (1.6%).

A mixture of 0.710 g. (2.02 mmoles) of triphenyltin hydride and 0.758 g. (8.90 mmoles) of methylene chloride was heated under reflux for 18 hr. Titration of the reaction mixture as above, required 9.25 ml. of 0.2000 *N* sodium hydroxide (92.0%).

In a separate experiment, 35.1 g. (0.1 mole) of triphenyltin hydride was mixed with 20.0 g. (0.24 mole) of methylene chloride and heated under reflux. The methyl chloride formed in the reaction was trapped in a tube cooled in a Dry Ice–acetone bath. The vapor phase chromatograph showed the presence of methyl chloride by comparison with a known sample. Further evidence for the presence of methyl chloride was obtained by collecting the gas in an infrared cell and comparing its spectrum with that known for methyl chloride, with which it was identical.

The Anomalous Hydrogenation of Carbomethoxyhydrazones[1]

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It has been reported[2] that monosubstituted hydrazines may be prepared in high yields from aldehyde or ketone carbethoxyhydrazones by catalytic hydrogenation, followed by hydrolyis of the resulting carbethoxyhydrazines. An attempt to apply this procedure to aldehyde carbomethoxyhydrazones led to unexpected results.

The hydrogenation of heptaldehyde carbomethoxyhydrazone in acetic acid produced an unknown crystalline solid, I, m.p. 71–72°, in addition to the desired substituted hydrazine. Catalytic reduction of acetaldehyde carbomethoxyhydrazone afforded similar results, and a compound, m.p. 111–112°, was formed along with crude 1-ethyl-2-carbomethoxyhydrazine.

Compound I, $C_{16}H_{34}N_2O_2$, was not attacked readily by 5% alcoholic potassium hydroxide solution, but was hydrolyzed to a chlorine containing substance, $C_{14}H_{33}ClN_2$, by refluxing with concentrated hydrochloric acid. This was shown to be 1,1-diheptylhydrazine hydrochloride by comparison with an authentic sample of the material which was prepared by the alkylation of hydrazine with *n*-heptyl chloride. These results suggested that I is 1-carbomethoxy-2,2-diheptylhydrazine.

In order to substantiate this structure, the

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(2) J. R. Geigy A.-G., Swiss Patent 307,629; *Chem. Abstr.*, **51**, 5113 (1957).