m. p. 132–134°. Its phenolic properties are very weak. In chloroform, $[\alpha]^{26}\text{D}$ −51.0° (c = 1.29).

Anal. Calcd. for $C_{24}H_{33}O_2N$: C, 78.42; H, 9.06. Found: C, 78.59; H, 9.06.

Cyclohexyltetrahydrodesoxycodeine.—In contrast to phenyldihydrodesoxycodeine, cyclohexyldihydrodesoxycodeine can be hydrogenated as base in methanol solution; the absorption (1 mole) is 25 times as fast when the hydrochloride with excess acid and methanol is hydrogenated in the presence of platinum oxide. Cyclohexyltetrahydrodesoxycodeine crystallizes from methanol, sublimes at 160° and 0.001 mm.; it is very weakly phenolic. The m. p. is 193–193.5°, $[\alpha]^{25}\text{D}$ −14.2° ($CHCl_3$, c = 1.34).

Anal. Calcd. for $C_{24}H_{35}O_2N$: C, 77.99; H, 9.55. Found: C, 77.90; H, 9.41.

Summary

1. Codeine derivatives having the pseudocodeine type of structure react with Grignard's reagent to give phenolic products containing the hydrocarbon group of the reagent.

2. Addition of organomagnesium halides to desoxycodeine-C takes place in at least two ways but the mechanism is not established.

3. Methyl- and ethyldihydrodesoxycodeines can be hydrogenated normally, but phenyldihydrodesoxycodeine, like phenyldihydrothebaine, resists hydrogenation. Under certain conditions it adds four moles of hydrogen, but the resulting hexahydrophenyltetrahydrodesoxycodeine is not the same as cyclohexyltetrahydrodesoxycodeine.

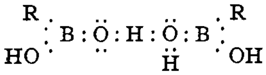
UNIVERSITY, VIRGINIA RECEIVED NOVEMBER 22, 1935

[CONTRIBUTION NO. 49 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

The Molecular Weights of the Organoboric Acids

BY CORLISS R. KINNEY AND DONALD F. PONTZ

According to the theory of hydrogen bond formation originally proposed by Latimer and Rodebush,[1] organoboric acids might be expected to form double molecules in a manner similar to the alcohols and to the carboxylic acids.



$$\begin{array}{ccccccccccccc} R & \cdot & & & & & & & & & & \cdot & R \\ & \vdots & B & : & \ddot{O} & : & H & : & \ddot{O} & : & B & \vdots & \\ HO & \cdot & & & \cdot\cdot & & & & \ddot{H} & & & \cdot & OH \end{array}$$

The application of the theory to the organoboric acids was tested experimentally by determining cryoscopically in nitrobenzene the molecular weights of several derivatives. Preliminary experiments showed that these substances have a tendency to dehydrate under the atmospheric conditions prevailing in Salt Lake City and that the products have high molecular weights. However, when the acids were freshly crystallized from water and had the proper empirical formula as evidenced by the boron analyses given in the accompanying table of data (halogen analyses are also included for those substances containing halogen) molecular weights were obtained which show that the organoboric acids are unimolecular in nitrobenzene.

TABLE I

Derivative of boric acid	Boron, % Calcd.	Boron, % Found		Halogen, % Calcd.	Halogen, % Found		Mol. wt. Calcd.	Mol. wt. Found	
Phenyl	8.88	8.63	8.69				121.9	127	131
p-Tolyl[a]	7.96	7.80	7.79				135.9	122	139
m-Chlorophenyl[a]	6.92	6.80	6.81	22.68	22.76	22.92	156.3	178	182
p-Chlorophenyl[a]	6.92	6.74	6.79	22.68	22.52	22.71	156.3	151	171
p-Bromophenyl	5.39	5.23	5.25	39.80	39.46	39.32	201.9	210	200
o-Phenethyl[a]	6.52	6.39	6.39				165.9	165	169
p-Phenoxyphenyl[a]	5.06	5.06	5.05				213.9	192	213
α-Naphthyl[a]	6.29	6.05	6.32				171.9	153	155

[a] Obtained from the Chemical Laboratory of the University of California through the courtesy of Dr. D. L. Yabroff.

Conclusions

An examination of the data demonstrates that the organoboric acids studied do not associate in nitrobenzene and that in this solvent there is no appreciable amount of hydrogen bond formation.

SALT LAKE CITY, UTAH RECEIVED NOVEMBER 6, 1935

---

[1] Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).