ing. N-Phenylcarbamyltaurine prepared according to Schoeberl[2] decomposed at 195–200° (corr.) without melting (Schoeberl, 195°).

Summary

Practical details have been described for convenient and inexpensive preparations of larger quantities of β-aminoethyl bromide hydrobromide and taurine in yields of 90 and 80%, respectively.

NEW YORK, N. Y. RECEIVED DECEMBER 4, 1935

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Addition of Organomagnesium Halides to Pseudocodeine Types. I. Desoxycodeine-C[1]

BY LYNDON SMALL AND KECHEE C. YUEN

Thebaine reacts with phenylmagnesium bromide to give a phenolic base, phenyldihydrothebaine,[2] of uncertain structure. The location of the phenyl group is not known, nor is there evidence to show whether structural changes other than scission of the ether linkage have taken place. Phenyldihydrothebaine is of particular theoretical interest because it is remarkably indifferent to catalytic hydrogenation,[3] although its empirical formula indicates that two alicyclic double linkages must still be present. The recently described methyldihydropseudocodeinone[4] shows a similar inexplicable reluctance toward reduction, whether catalytic or by metal combinations.

In the belief that the ability of thebaine to react with organomagnesium halides depends upon the conjugation of the 6,7-double bond with the ether oxygen in a system resembling that of an α,β-unsaturated ketone,[5] we have undertaken a study of the parallel reaction of other bases containing this grouping. Desoxycodeine-C was chosen as the simplest available representative of the type; the extension of the study to the phenyldihydrothebaine problem will be described in other communications.

Desoxycodeine-C (II),[6] though containing no group obviously open to attack by Grignard's reagent, reacts with methylmagnesium iodide to yield a phenolic product, methyldihydrodesoxycodeine, differing in composition from the starting material by CH_4. The desoxycodeine methoxyl group is still present, and the appearance of the phenolic hydroxyl proves that the ether-linked oxygen of desoxycodeine-C is involved in the reaction. Only two modes of addition of RMgX to the system appear to come into question: a 1,4-addition, comparable to that observed with many α,β-unsaturated ketones, which would locate the entering methyl group at C-7 of the phenanthrene skeleton (III); or a 1,2-addition, facilitated by an activating influence of the double bond on the ether linkage similar to that which undoubtedly operates in certain reduction reactions. The 1,2-mechanism would locate the methyl group on C-5 (IV),[7]

A decision between the 5- and 7-positions must rest on degradation to known phenanthrene derivatives. Zinc-dust distillation of methyldihydrodesoxycodeine gave as the principal indifferent product a colorless liquid, the picrate of which could be separated into two apparently homogeneous fractions. One of these had the melting point of 2-(or 7)-methylphenanthrene picrate, the other that of 4-(or 5)-methylphenanthrene picrate.[8] Both of these gave melting-point depressions with authentic samples generously supplied by Dr. Haworth, and may be products of incomplete

(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

(2) Freund, *Ber.*, **38**, 3284 (1905); Freund and Speyer, *ibid.*, **49**, 1287 (1916); German Patent 181,510 (1907), also mentions the reaction of benzylmagnesium chloride.

(3) Hoek, Dissertation, Munich, 1926; verified in this Laboratory.

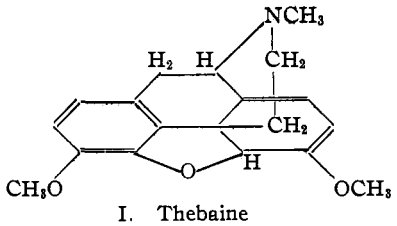
(4) Lutz and Small, THIS JOURNAL, **57**, 2651 (1935).

(5) Bases of the morphine series having the alicyclic unsaturation in the 7,8-position, for example codeine methyl ether, are unaffected by prolonged treatment with methylmagnesium iodide.

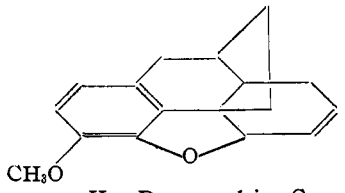
(6) Small and Cohen, THIS JOURNAL, **53**, 2214 (1931); Small and Morris, *ibid.*, **55**, 2874 (1933).

(7) In contrast to thebaine and other unsaturated morphine bases, phenyldihydrothebaine shows no tendency to lose the entire ethanamine side chain in degradation reactions; to account for this, it has been suggested that the phenyl group may occupy a position such that it blocks aromatization (*i. e.*, C-14) (Small and Lutz, "Chemistry of the Opium Alkaloids," p. 333). Unless a 1,6-addition of RMgX to thebaine be conceded, a reaction mechanism leading to such a result is not obvious, and in the case of desoxycodeine-C can scarcely be considered.

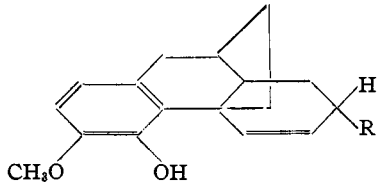
(8) Haworth, *J. Chem. Soc.*, 1125 (1932).



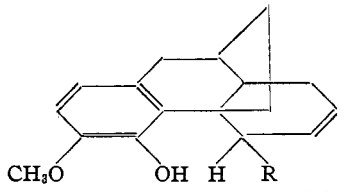
I. Thebaine



II. Desoxycodeine-C



III. 7-Alkyldihydrodesoxycodeine



IV. 5-Alkyldihydrodesoxycodeine

degradation. A solid crystalline hydrocarbon obtained in small yield from the degradation yielded analytical values corresponding to methylphenanthrene, but had different physical properties from any of the five known methylphenanthrenes. The question of reaction mechanism will therefore be carried over into another, more accessible series.

Whichever mechanism operates in the addition, an asymmetric carbon atom is generated at C-5 or C-7, and the formation of diastereomers is possible. In the case of the methyl derivative, only one compound could be isolated; in the reaction of desoxycodeine-C with ethylmagnesium iodide, isomeric ethyldihydrodesoxycodeines (one of which was isolated only after hydrogenation) were formed. The isomerism may be due to a configurational, or a positional, difference for competing 1,2- and 1,4-addition of RMgX is not excluded. In addition to the isomers mentioned, a small amount of two high-melting bases of unknown nature was isolated. Both methyl- and ethyldihydrodesoxycodeine could be hydrogenated readily in organic media, although the reaction proceeded about one hundred times as fast in the presence of a little hydrochloric acid.[9]

The reaction between desoxycodeine-C and phenylmagnesium bromide gives phenyldihydrodesoxycodeine. This base is very weak in its phenolic character in comparison with the methyl and ethyl derivatives; in contrast to them, it cannot be hydrogenated under ordinary conditions, and recalls in this respect the anomalous behavior of phenyldihydrothebaine. The peculiarity of phenyldihydrodesoxycodeine toward catalytic reduction cannot be explained as a steric hindrance effect, for cyclohexyldihydrodesoxycodeine behaves normally; furthermore, in so far as inferences may be drawn from evidence in the thebaine series, the abnormality cannot be ascribed to the influence of the "negative" phenyl group, for we have not yet been able to hydrogenate any member of a series of methyldihydrothebaines recently obtained in this Laboratory (Mr. E. M. Fry).

Addition of phenylmagnesium bromide to desoxycodeine-C proceeds to at least 83% in one way. A positional or configurational isomer could not be isolated as such, but from hydrogenation of the mother liquors a small amount of a phenyltetrahydrodesoxycodeine was obtained. This substance must be derived from a phenyldihydrodesoxycodeine different from the one discussed above, which cannot be dihydrogenated under any conditions.

Only when hydrogenated in alcohol with excess of acid does phenyldihydrodesoxycodeine add hydrogen, and then not two atoms, but eight. The resulting hexahydrophenyltetrahydrodesoxycodeine shows no detectable phenolic properties, but the effect of hydrogenation of ring III in weakening the acidity of the 4-hydroxyl has been observed in several series of morphine derivatives. A reduction of aromatic ring I of the morphine nucleus has never been realized, and need hardly be discussed; the alicyclic double linkage in ring III of phenyldihydrodesoxycodeine appears to be so located that its reduction inevitably involves the new aromatic nucleus. Hexahydrophenyltetrahydrodesoxycodeine should therefore be identical with cyclohexyltetrahydrodesoxycodeine. The latter compound was prepared by hydrogenation of cyclohexyldihydrodesoxycodeine, from interaction of cyclohexylmagnesium chloride and desoxycodeine-C, and was found to be different

(9) Acceleration of hydrogenation by hydrochloric acid, see Packendorff, *Ber.*, **67**, 905 (1934).

from hexahydrophenyltetrahydrodesoxycodeine. Whether the difference lies in the mode of addition of the phenyl and cyclohexyl groups or in a false concept concerning the hydrogenation of phenyldihydrodesoxycodeine cannot be demonstrated.

Experimental

Methyldihydrodesoxycodeine.—Desoxycodeine-C, prepared by the method of Small and Cohen, was purified through the salicylate, which has not previously been described. The salt crystallizes from alcohol, distils without decomposition in high vacuum at 135°, and has the m. p. 195–196°; in alcohol $[\alpha]^{24}_D$ −112.2° (c = 1.675).

Anal. Calcd. for $C_{18}H_{27}O_3N$: C, 71.22; H, 6.46. Found: C, 71.24; H, 6.54.

A solution of 10 g. of desoxycodeine-C in 200 cc. of absolute ether was treated with 130 cc. of molar methylmagnesium iodide and heated under reflux for ten and one-half hours. The insoluble magnesium complex was decomposed with 10% acetic acid, the base liberated in the aqueous layer with ammonia in the presence of a trace of sodium hydrosulfite, and shaken into chloroform. When rubbed up with methyl alcohol the residue from the chloroform yielded 5.7 g. of methyldihydrodesoxycodeine (55% yield). Hydrogenation of the mother liquor gave 1.4 g. of tetrahydrodesoxycodeine, arising from unreacted desoxycodeine-C.

Methyldihydrodesoxycodeine crystallizes from methanol or methyl acetate, often in a solvated form melting below 100°; this form changes rapidly to the stable solvent-free form, m. p. 145–146°. It sublimes at 125° and 0.001 mm. In alcohol or chloroform, $[\alpha]^{25}_D$ +69.7° (c = 1.09). The base is precipitated when alkali is added to its solution in acids, and redissolves in an excess of alkali; ammonium chloride or carbon dioxide reprecipitates it from the alkaline solution.

Anal. Calcd. for $C_{19}H_{25}O_2N$: C, 76.20; H, 8.42; OCH_3, 10.37. Found: C, 76.23; H, 8.69; OCH_3, 10.33.

Degradation of Methyldihydrodesoxycodeine.—A mixture of 8.2 g. of methyldihydrodesoxycodeine with 75 g. of zinc dust was distilled over 40 cm. of zinc dust on pumice at dull red heat, in a stream of hydrogen. The brown half-solid tar was dissolved in ether, and washed with dilute hydrochloric acid, then with dilute sodium hydroxide, whereby most of the color was removed. The oily residue remaining after distillation of the ether was distilled at 100° (0.01 mm.), yielding a yellow oil and a short crystalline layer. The oily portion (0.16 g.) formed a picrate which could be fractionated from alcohol into two portions, m. p. 118–119°, m. p. 138–141°, which, respectively, gave depressions of about 10° in m. p. when mixed with samples of 2- and 4-methylphenanthrene picrates supplied by Dr Haworth. The crystalline fraction (0.20 g.), after three distillations at 125° (17 mm.) was crystallized twice from alcohol; feathery white flakes, 15 mg., m. p. 103° (unsharp, sintering from 95°).

Anal. Calcd. for $C_{15}H_{12}$: C, 93.70; H, 6.30. Found: C, 93.85; H, 6.62.

The picrate prepared from it crystallized in long yellow needles, and melted at 95–98° (sintering from about 85°).

Methyltetrahydrodesoxycodeine.—Hydrogenation of methyldihydrodesoxycodeine in the form of base or as hydrochloride resulted in absorption of one mole of hydrogen and formation of methyltetrahydrodesoxycodeine. The base crystallizes from dilute methanol, often separating solvated. The solvent-free form melts at 128–129° and has $[\alpha]^{25}_D$ −47.8° (alcohol, c = 1.042). Its phenolic character is less pronounced than that of the unhydrogenated derivative.

Anal. Calcd. for $C_{19}H_{27}O_2N$: C, 75.70; H, 9.04. Found: C, 75.88; H, 8.79.

α-Ethyldihydrodesoxycodeine.—An absolute ethereal solution of 11 g. of desoxycodeine-C was treated with 240% excess of ethylmagnesium iodide as described for the methyl derivative. After decomposition of the magnesium complex the major portion of the product was extracted into ether; the remainder (36%) was extracted into chloroform, from which no crystalline material could be obtained. The residue from the ether extract yielded on treatment with acetone 3.5 g. of α-ethyldihydrodesoxycodeine, purified from acetone, m. p. 156–164°. Purification through salts, or sublimation (125° at 0.001 mm.) did not change the m. p. or rotation, $[\alpha]^{22}_D$ −184.2° ($CHCl_3$, c = 1.10). The phenolic properties are somewhat weaker than those of the methyl derivative.

Anal. Calcd. for $C_{20}H_{27}O_2N$: C, 76.62; H, 8.69. Found: C, 76.52; H, 8.88.

α-Ethyltetrahydrodesoxycodeine.—Hydrogenation of α-ethyldihydrodesoxycodeine with absorption of 1 mole of hydrogen (platinum oxide) proceeded slowly in methanol, over 100 times as fast in dilute methanol with excess of normal hydrochloric acid. The tetrahydro derivative is sparingly soluble in methanol or acetone, sublimes at 125° and 0.001 mm., and is weakly phenolic. Its m. p. is 168.5–169°, $[\alpha]^{23}_D$ −54.8° ($CHCl_3$, c = 1.131).

Anal. Calcd. for $C_{20}H_{29}O_2N$: C, 76.13; H, 9.27. Found: C, 76.04; H, 9.19.

β-Ethyltetrahydrodesoxycodeine.—The acetone mother liquors from the isolation of α-ethyldihydrodesoxycodeine yielded 4.2 g. of an oil which gave no crystalline salts. In methanol with platinum oxide it absorbed 395 cc. of hydrogen. Evaporation of the methanol and treatment with acetone gave 0.55 g. of crystals, from which by sublimation at 130° and 0.001 mm., 0.53 g. of pure β-ethyltetrahydrodesoxycodeine and 0.02 g. of unidentified organic residue (not melted at 350°) was obtained. From the acetone mother liquor a second crop (30 mg.) of needles, m. p. 215–216°, unidentified, could be separated.

β-Ethyltetrahydrodesoxycodeine crystallizes best from acetone, and has the m. p. 148–153°; $[\alpha]^{26}_D$ −37.6° ($CHCl_3$, c = 0.943); weakly phenolic. It depressed the m. p. of α-ethyltetrahydrodesoxycodeine by 30°.

Anal. Calcd. for $C_{20}H_{29}O_2N$: C, 76.13; H, 9.27. Found: C, 75.94; H, 9.34.

Phenyldihydrodesoxycodeine.—The reaction of 5.5 g. of desoxycodeine-C with 70 cc. of molar phenylmagnesium bromide according to the foregoing procedure gave from the chloroform extract 5.2 g. of crystalline phenyldihydrodesoxycodeine, and 0.8 g. of unchanged desoxycodeine-C (isolated as salicylate). From the salicylate mother liquors 0.7 g. of an oily base (mixed with some phenol) was

isolated. This was hydrogenated, and yielded 130 mg. of crystals, purified from dilute methanol and by sublimation, m. p. 218–220°, which appeared to be a phenyltetrahydrodesoxycodeine; in chloroform $[\alpha]^{26}D$ +16.1° (c = 0.622).

Anal. Calcd. for $C_{24}H_{29}O_2N$: C, 79.29; H, 8.05. Found: C, 79.74; H, 8.25.

Phenyldihydrodesoxycodeine is sparingly soluble in organic media excepting chloroform, but can be recrystallized from ethyl acetate. It sublimes at 175° and 0.001 mm.; it is very slightly soluble in alkali and precipitated by ammonium chloride. It melts at 184.5–185.5° and has $[\alpha]^{24}D$ +129.3° ($CHCl_3$, c = 1.47).

Anal. Calcd. for $C_{24}H_{27}O_2N$: C, 79.73; H, 7.53. Found: C, 79.66; H, 7.81.

Hexahydrophenyltetrahydrodesoxycodeine. — Phenyldihydrodesoxycodeine absorbs no hydrogen in methanol with platinum oxide, in absolute ethanol with palladium–charcoal, or as acetate in aqueous solution with palladium–barium sulfate. A solution of 1.04 g. of base in 10 cc. of normal hydrochloric acid and 50 cc. of methanol with 0.15 g. of platinum oxide absorbed 286 cc. (corrected) in twenty-five hours, 55% being absorbed in the first hour; for four moles, calcd., 252 cc. The product was worked into ether solution in the usual way, and crystallized by addition of acetone to the residue from ether distillation. It is very soluble in most solvents, and was purified by slow addition of water to a hot acetone solution. The m. p. is 132–134°, $[\alpha]^{24}D$ −48.4° ($CHCl_3$, c = 1.571). Phenolic properties cannot be demonstrated by alkali solubility.

Anal. Calcd. for $C_{24}H_{35}O_2N$: C, 77.99; H, 9.55. Found: C, 77.72; H, 9.50.

Cyclohexyldihydrodesoxycodeine.—An ethereal solution of 6.8 g. of desoxycodeine-C did not react with 150 cc. of 0.6 molar cyclohexylmagnesium chloride on refluxing for twenty-seven hours. The reaction was continued in isoamyl ether at 100° for twelve hours. The magnesium complex was worked up in the usual way, resulting in a dark oil from concentration of the chloroform extract. This was treated with 25 cc. of 25% aqueous perchloric acid and 25 cc. of ethanol, heating to clear solution. The yield of crude crystalline perchlorate was 6.8 g. It was washed with ether and the base isolated in the usual way. It was recrystallized from a mixture of 80% isopropyl ether–20% methyl alcohol. The base melts at 131.5–132.5°, and sublimes at 140° and 0.001 mm. It depresses the m. p. of hexahydrophenyltetrahydrodesoxycodeine of

TABLE OF DERIVATIVES

V, Methyldihydrodesoxycodeine
VI, Methyltetrahydrodesoxycodeine
VII, α-Ethyldihydrodesoxycodeine
VIII, α-Ethyltetrahydrodesoxycodeine
IX, Phenyldihydrodesoxycodeine
X, Hexahydrophenyltetrahydrodesoxycodeine
XI, Cyclohexyldihydrodesoxycodeine
XII, Cyclohexyltetrahydrodesoxycodeine

Derivative	Formula	M. p., °C.	$[\alpha]^{\circ}D$	t	c	Solvent		Calcd.	Found
V-Hydriodide[a]	$C_{19}H_{26}O_2NI$	155–158	+ 51.9	23	1.08	$CHCl_3$	I	29.71	29.53
V-Hydrobromide[b]	$C_{19}H_{26}O_2NBr$	245–246	+ 61.5	23	1.15	$CHCl_3$	Br	21.02	20.65
V-Methiodide[c]	$C_{20}H_{28}O_2NI$	239	+ 28.8	25	1.27	$CHCl_3$	I	28.77	28.63
VI-Hydrochloride[d]	$C_{19}H_{28}O_2NCl$	240.5	− 23.1	25	0.86	$CHCl_3$	Cl	10.50	10.06
VI-Hydrobromide[e]	$C_{19}H_{28}O_2NBr$	248–249	− 21.9	22	1.18	$CHCl_3$	Br	20.91	20.41
VI-Methiodide[f]	$C_{20}H_{30}O_2NI + C_2H_5OH$	254–255	− 34.9	25	1.63	$CHCl_3$	C_2H_6O	9.41	9.55
							I	25.94	25.88
VII-Hydriodide[g]	$C_{20}H_{28}O_2NI$	205–210	−123.2	23	1.15	EtOH	I	28.77	29.20
VII-Perchlorate[h]	$C_{20}H_{28}O_6NCl$	187–200	−134.7	26	1.17	EtOH	Cl	8.57	8.56
VII-Methiodide[i]	$C_{21}H_{30}O_2NI$	210–215	−111.4	26	1.60	EtOH	I	27.88	27.97
VIII-Hydriodide[j]	$C_{20}H_{30}O_2NI$	234	− 2.9	24	2.22	$CHCl_3$	I	28.64	28.92
IX-Picrate[k]	$C_{30}H_{30}O_9N_4 + H_2O$	129–132[r]	+ 69.5	20	1.13	$CHCl_3$	H_2O	2.96	3.00
							N	9.49[r]	9.68
IX-Benzoate[l]	$C_{31}H_{33}O_4N$	203–204	+ 82.1	24	0.62	EtOH	C	76.98	76.99
							H	6.88	7.10
IX-Methiodide[m]	$C_{25}H_{30}O_2NI$	257.5–258	+105	25	.24	EtOH	I	25.22	25.34
X-Perchlorate[n]	$C_{24}H_{36}O_6NCl$	255–256	− 16.7	26	1.02	EtOH	Cl	7.55	7.40
X-Methiodide[o]	$C_{25}H_{38}O_2NI$	250	− 28.0	25	1.03	$CHCl_3$	I	24.83	24.58
XI-Perchlorate[p]	$C_{24}H_{34}O_6NCl$	250–251	− 26.3	25	1.37	$CHCl_3$	Cl	7.58	7.27
XII-Hydriodide[q]	$C_{24}H_{36}O_2NI$	235–236	+ 14.8	23	0.95	$CHCl_3$	I	25.53	25.72

[a] Prepared in the usual way, crystallized from water. [b] Crystallizes from water, very soluble in alcohol; six-sided plates. [c] Prepared in, and crystallized from acetone; very soluble in water. [d] Prepared with 3 *N* hydrochloric acid, crystallizes as flat needles from acetone. [e] Prepared with 4 *N* hydrobromic acid, purified from water. [f] Prepared in acetone, purified from alcohol. [g] Crystallized from 50% alcohol. [h] Prepared in alcohol with 25% perchloric acid, crystallizes as six-sided prisms from 50% alcohol. [i] Prepared in hot benzene, crystallized from water, sensitive to light. [j] Difficultly soluble in water, soluble in methanol or ethanol, purified from 20% methanol. [k] Yellow rectangular crystals from alcohol; hydrated form melts with gas evolution at about 115°. [l] Prepared in alcohol, recrystallized from 1:1 alcohol–ether mixture. [m] Prepared in hot benzene, crystallizes from alcohol in rectangular flakes. [n] Prepared with 25% perchloric acid, recrystallized by addition of water to an alcohol solution. [o] Prepared in acetone, recrystallized from 10 parts of alcohol. [p] Prepared with 10% perchloric acid, recrystallized by dissolving in alcohol and adding water. [q] Recrystallized by adding water to a hot alcohol solution. [r] Anhydrous.

m. p. 132–134°. Its phenolic properties are very weak. In chloroform, $[\alpha]^{26}D$ −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°, $[\alpha]^{25}D$ −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.

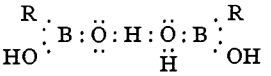
UNIVERSITY, VIRGINIA RECEIVED NOVEMBER 22, 1935

[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.



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.	Found		Halogen, % Calcd.	Found		Mol. wt. Calcd.	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.

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

SALT LAKE CITY, UTAH RECEIVED NOVEMBER 6, 1935