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Effect of 1,3-Diol Structure on the Distribution of Boron Between $CHCl_3$ and Aqueous Phase

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Effect of 1,3-Diol Structure on the Distribution of Boron Between $CHCl_3$ and Aqueous Phase

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ABSTRACT

The various new aliphatic 1,3-diols, containing primary, secondary, tertiary, and mixed of these groups, were synthesized and used for the solvent extraction of boron. Diols (**8a**, **8b**, **9**, **10a**, **10b**, **11**, **12a**, **12b**, **13**) were prepared from (β-hydroxy carbonyl compounds **1**–**7**. The fixed standard solution of boric acid of 1.00×10^{-2} M was extracted with 0.1 M and 0.5 M diols at equilibrium pH of 2 and at constant ionic strength ($I = 0.5$). The best extracting reagent was found to be **11**, which is a primary–tertiary class of -OH groups and methyl groups as a substituent on the second carbon of 1,3-diol.

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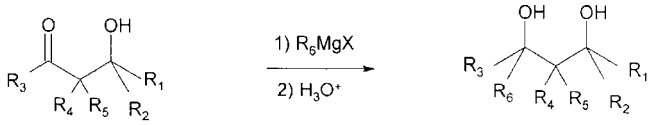
INTRODUCTION

Boron concentration in aqueous medium may vary widely, for example from 5 parts per million (ppm) to 1 molar, depending on the source. In many natural and artificial waters and brines, and in dilute solutions from many processes, boron is often present in relatively low concentrations. It is desirable to remove boron from such solutions for purification purposes, such as removal of boron contamination from irrigation waters. In some places, large amounts of waters are not suitable for irrigation because the boron content exceeds 2 or 3 ppm, which is the tolereable limit for citrus and some other agricultural crops.[1] This problem is beginning to reach significant proportions at three large-scale operations in Turkey where there is a danger of severe pollution in the not-too-distant future.[2–4]

Boron contamination is commonly present in magnesium chloride brines, and it interferes with the subsequent production of magnesium metal by electrowinning operations. It is desirable to remove boron contamination in many other situations as well. The quantity of boron that may be contained in some brines is an economical source of relatively high purity boron compounds, preferably boric acid, which has a relatively high marked value compared for example, with borax.[5]

Various materials have been employed for extracting boron, such as β-aliphatic diols[5–9] or certain catechols[10,11] and other boron extractants.[12] Besides other 1,3-diols, 1.2-, and 1,4-dihydroxy, diketo, ketohydroxy, aminohydroxy, and diamino compounds were investigated. Extraction ability and distribution values of various 1,3-diols, carbon numbers change between 4–15 and have different classes (1°-1°, 1°-2°, 2°-2°, and 2°-3°) were investigated but not in detail by Egneus and Uppström.[13]

Many studies have been conducted on 1,3-diol extractants, but these do not depend on the classes of diols. Our objective was to synthesize various 1,3-diol extractants for both recovery and removal of boron by liquid–liquid extraction, known as the most economical technique for boron. So in this study various 1,3-diols were synthesized (Sch. 1), containing primary, secondary, tertiary, and mixed classes of 1,3-diols which were limited to their carbon number between 11 and 14. In the present study, depending on the classes of different of 1,3-diols extraction ability and distribution values were investigated in detail, but properties not considered with respect to their stripping facility and selectivity. Many different methods have been reported based on the synthesis of 1,3-diols.[14–23] However, in this study a simple general synthesis procedure was developed so that new, aliphatic 1,3-diols were synthesized by the reaction of some β-hydroxy carbonyl compounds with appropriate Grignard reagents (see Table 1).



1 R_1=R_2=R_3: CH_3, R_4=R_5: H
(4-Methyl-4-hydroxy-2-pentanon)

2 R_1=R_3: CH_3, R_2=R_4=R_5: H
(4-Hydroxy-2-pentanone)

3 R_1: CH_3, R_2=R_3=R_4=R_5: H
(3-Hydroxybutanal)

4 R_3=R_5: CH_3, R_1=R_2=R_4: H
(4-Hydroxy-3-methyl-2-butanone)

5 R_4=R_5: CH_3, R_1=R_2=R_3: H
(2,2-Dimethyl-3-hydroxypropanal)

6 R_4=R_5: CH_3, R_1=R_2=R_3: H -OH= -OTHP
(2,2-Dimethyl-3-tetrahydropyranyloxipropanal)

7 R_1=R_2=R_3= R_4= R_5: H -OH= -OTHP
(3-Tetrahydropyranyloxipropanal)

8a R_6: Benzyl, **8b** R_6: Octyl

9 R_6: Benzyl

10a R_6: Benzyl, **10b** R_6: Octyl

11 R_6: Benzyl

12a R_6: Benzyl, **12b** R_6: Octyl

12b R_6: Octyl

13 R_6: Octyl

Scheme 1.

EXPERIMENTAL

Apparatus

IR spectra were recorded on a Midac 1700 instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively on a Bruker AC spectrometer in $CDCl_3$. Spectra are reported in ppm (δ) downfield from internal Me_4Si. Elemental analyses were performed on a Carlo Erba Model 1108 instrument. The equilibrium pH was measured by Danver's Basic pH meter. Boron concentrations in aqueous phase were determined spectrometrically by Unicam Uv2 Uv-visible spectrophotometer.

Synthesis of 1,3-Diol Extractants

2-Benzyl-4-metil-2,4-pentanediol (8a): Under nitrogene atmosphere and in an ice bath 0.6 mole of benzylmagnesium bromide in dry ether (100 mL) was prepared in a 500 mL three-necked flask, fitted with reflux condenser,

Table 1. Synthesis of 1,3-diols by reaction of Grignard reagents with β-hydroxy carbonyl compounds.

β-hydroxy carbonyl	1,3-Diol	Bp (°C)/ mm Hg	n_{Di}^{20}	Yield %	Elemental analysis (calculated found) C%	H%
1[a]	**8a**	114–116/0.1	1.513	50	71.28/71.31	12.87/12.98
1[a]	**8b**	112–114/0.1	1.447	38	73.04/73.10	13.04/13.10
2[b]	**9**	108–110/0.85	1.519[c]	67	74.23/74.30	9.28/9.31
3[d]	**10a**	112–114/0.1	1.510	38	73.30/74.36	9.98/10.01
3[d]	**10b**	111–113/0.1	1.446	49.5	74.23/74.28	9.28/9.38
4[e]	**11**	138–140/0.7	–[f]	65.7	74.23/74.30	9.28/9.30
5[g]	**12a**	138–140/0.7	–[h]	69	74.23/74.30	9.28/9.30
5[g]	**12b**	110–112/0.1	1.452	58.4	72.22/72.28	12.96/13.10
6[i]	**12b**	–	–	43	–	–
7[j]	**13**	110–112/0.1	1.450	43	70.21/70.18	12.76/12.85

[a] Bp_{23} 71–74°C, n_{Di}^{25} 1.4213.[24]
[b] Bp_{25} 85–88°C, n_{Di}^{25} 1.4250.[20]
[c] t = 33°C.
[d] Beil. Ref. 4-01-00-03310, bp_{23} 41–42°C.
[e] bp_{25} 85–88°C, n_{Di}^{20} 1.4310.[15]
[f] mp 66–67°C.
[g] Beil. Ref. 1, IV, 4015, $bp_{0.1}$ 52–53°C.
[h] mp 85–86°C.
[i] Compound **5** was protected as described by Kozluk.[25]
[j] **7** was synthesized as described by Kitching,[26] bp_{01} 46–47°C.

stirrer, and dropping funnel. 4-metyl-4-hydroxy-2-pentanon (**1**) (29 g, 0.25 mole) in 70 mL of dry ether was added to the flask in period of 1.5 hr. Then it was allowed to warm to room temperature and stirred for an additional 1 hr. The mixture was decomposed on an ice bath by saturated aqueous ammonium chloride. After drying over sodium sulfate, the ether solution was concentrated by evaporation. Crude product was distilled to give 26 g (50%) of 2-benzyl-4-metil-2,4-pentanediol.

2,4-Dimethyl-2,4-dodecanediol (8b): As described in the above experiment using 0.6 mole of octylmagnesium bromide and 4-metyl-4-hydroxy-2-pentanon (**1**) (29 g, 0.25 mole) yielded 22 g (38 %) of 2,4-dimethyl-2,4-dodecanediol.

2-Benzyl-2,4-pentanediol (9): As described above experiment using benzylmagnesiumchloride (0.133 mole) and 4-hydroxy-2-pentanon (**2**) (3.77 g, 0.037 mole) yielded 4.85 g (67%) of 2-benzyl-2,4-pentanediol.

1-Benzyl-1,3-butanediol (10a): Benzylmagnesiumchloride (0.6 mole) and β-Hydroxybutanal (**3**) (22 g, 0.25 mole) were treated as described in the above experiment and distilled product was purified by silica gel column chromatography with hexane:ether (2:1) and redistilled to give 17.1 g (38%) of 1-benzyl-1,3-butanediol.

2,4-Dodecanediol (10b): Octylmagnesium bromide (0.25 mole) and (8.8 g, 0.1 mole) of **3** were treated as described in above experiment and distilled product was purified by silica gel column chromatography with hexane:ether (2:1) and redistilled to give 10 g (49.5%) of 2,4-dodecanediol.

2-Methyl-3-benzyl-1,3-butanediol (11): As described in above experiment using benzylmagnesium-chloride (0.3 mole) and 4-Hydroxy-3-methyl-2-butanone (**4**) (9.6 g 0.094 mole) yielded 12 g (65.71%) of 2-methyl-3-benzyl-1,3-butanediol.

2,2-Dimethyl-1-benzyl-1,3-propanediol (12a): As described in above experiment using benzylmagnesiumchloride (0.3 mole) and 2,2-dimethyl-3-hydroxypropanal (**5**) (9.2 g, 0.1 mole) yielded 13 g (69%) of 2,2-dimethyl-l-benzyl-1,3-propanediol.

2,2-Dimethyl-1,3-undecanediol (12b): As described in above experiment using octylmagnesium bromide (0.28 mole) and 2,2-dimethyl-3-hydroxypropanal (**5**) (11.5 g, 0.125 mole) yielded 14 g (58.4%) of 2,2-dimethyl-1,3-undecanediol. **By second method**: Octylmagnesium bromide (0.067 mole) and 2,2-dimethyl-3-α-tetrahydropyranyloksi-propanal (**6**) (8 g, 0.05 mole) were treated as described in above method. Crude product was deprotected using 0.1 mL of concentrated HCl in methanol (8 mL) by magnetically stirring for 36 hr, then neutralizing by $NaHCO_3$. Solvent evaporated and product was purified by distillation to give 4 g (43%) of 2,2-dimethyl-1,3-undecanediol.

1,3-Undecanediol (13): Octylmagnesium bromide (0.067 mole) and 3-α-tetrahydropyranyl-oksipropanal (**7**) (8 g, 0.05 mole) were treated using the method described above. Crude product was deprotected by using 0.12 mL of concentrated HCl in methanol (10 mL) by magnetically stirring for 36 hr, then neutralizating with $NaHCO_3$. Solvent evaporated and crude product was distilled to give 4 g (43%) of 1,3-undecanediol.

Elemental analyses and spectral data are in agreement with structures of all diols proposed (see Table 2).

Table 2. Spectral data of 1,3-diols.

1,3-Diols	IR (cm^{-1})	^{13}C NMR ($CDCl_3$)	^{1}H NMR ($CDCl_3$)
8a	3368, 3085, 3061, 3027, 2970, 2932, 1947, 1874, 1807, 1602, 1453, 1376, 1173, 939, 980, 742	137.95, 131.16, 128.48, 126.82, 74.31, 72.45, 51.44, 51.22, 33.18, 31.65, 28.99	7.3–74 (m, 5H); 3.83 (bs, 1H); 3.45 (bs, 1H); 2.82–3.04 (dd, 2H); 1.98–1.76 (dd, 2H); 1.42 (s, 3H); 1.38 (s, 3H); 1.38 (s, 3H)
8b	3330, 2925, 2854, 1467, 1415, 1376, 1193, 1174, 965, 893, 760.	74.40, 72.35, 50.39, 32.72, 32.18, 31.78, 30.54, 29.91, 29.59, 29.07, 24.57, 22.92, 14.33.	4.53 (bs, 1H); 4.29 (bs, 1H), 1.56–1.75 (dd,2H); 1.53–1.4 (m, 3H); 1.06–1.41 (m, 21H); 0.87 (t, 6.79 Hz, 2H)
9	3330, 3085, 3062, 3027, 2967, 2931, 1606, 1490, 1451, 1374, 1170, 1131, 1031, 942, 742, 730, 701	138.25, 137.94, 131.16, 130.94, 128.55, 128.50, 126.83, 126.80, 74.33, 74.08, 72.47, 65.69, 51.43, 51.24, 48.67, 46.98, 33.17, 31.65, 29.23, 28.98, 24.70	7.03–7.30 (m, 5H): 4.11–4.33 (m,1H); 3.85 (bs, 1H); 3.51 (bs, 1H); 2.95 – 2.62 (ddd, 2H); 1.57–1.82 (m, 8H)
10a	3364, 3062, 3027, 2967, 2932, 1700, 1495, 1454, 1374, 1318.9, 1127, 1084, 749, 700	140.85, 140.41, 131.64, 131.58, 130.58, 130.56, 128.51, 128.44, 75.58, 71.92, 70.60, 67.03, 46.75, 46.19, 45.98, 45.30, 25.98, 25.61	7.02–7.33(m, 5H); 3.5–4.18 (m, 2H); 3.70 (bs, 1H); 3.5 (bs, 1H); 2.60–2.82 (m, 2H); 1.50–1.78 (m, 2H); 1.15–1.24 (m, 3H)

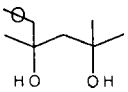
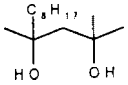
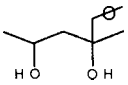
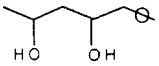
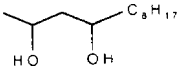
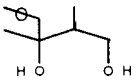
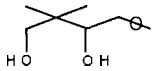
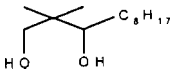
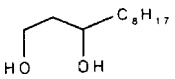
Table 2. Continued.

1,3-Diols	IR (cm^{-1})	^{13}C NMR ($CDCl_3$)	^{1}H NMR ($CDCl_3$)
10b	3369, 2927, 2954, 1463, 1376, 1318, 1144.3, 1124.3, 1084.4, 932, 830,721	72.89, 69.12, 68.96, 65.19, 44.90, 44.79, 38.48, 37.81, 32.20, 30.07, 30.03, 29.94, 29.92, 29.62, 29.60, 26.18, 25.74, 24.25, 23.72, 22.94, 14.32	3.86–4.11 (m, 4H); 1.17–1.56 (m, 19H); 0.88 (t. 6.75 Hz, 3H)
11	3366, 3084, 3059, 3028, 2972, 2928, 1603, 1495, 1453, 1375, 1304, 1151, 1082, 1019, 943, 727, 702, 645, 523	137.13,136.77, 130.39, 127.70, 127.66, 126.04, 125.94, 75.89, 75.39, 65.30, 65.19, 46.91, 43.17, 42.49, 41.65, 25.83, 21.55, 12.67, 12.38	7.24–7.37(m, 5H); 3.98(bs. 1H); 3.62–3.80(m, 2H); 3.26–3.32(bs, 1H); 2.65–2.90(m. 2H); 1.85–1.90(m. 1H); 1.12(s. 1.5H); 1.11(s, 1.5H); 1.02(d. 7.3 Hz. 1.5H): 0.92(d, 7.07 Hz, 1.5H)
12a	3352, 3084, 3067, 3028, 2955, 2934, 2869, 1494, 1471, 1454, 1404, 1171, 1078, 1065, 1042, 894, 857, 732, 507	139.01, 129.01, 128.16, 125.97, 79.52, 71.52, 38.10, 38.07, 22.23, 18.44	7.22–7.35(m, 5H), 3.41–3.69(m, 4H); 2.78(bs, 1H); 2.49–2.95(m, 2H); 0.98(s, 6H)
12b	3343, 2957, 2872, 1457, 1379, 1324, 1122, 1040, 981	79.61, 72.49, 38.67, 32.24, 32.07, 30.11, 30.00, 29.68, 27.11, 22.95, 22.96, 19.11, 14.38	4.17(bs, 1H); 3.8(bs, 1H); 3.36–3.52(m, 3H); 1.17–1.71(m, 14H); 0.88(t, 6.37 Hz, 3H); 0.86(s, 3H); 0.84(s, 3H)
13	3346, 2930, 2854, 1657, 1463, 1377, 1330, 1194, 1129, 1056, 968,721	71.16, 60.85, 38.91, 38.03, 32.19, 30.07, 29.94, 29.63, 25.98, 22.94, 14.30.	3.95–3.40(dbs, 2H); 3.71–3.80(m, 3H); 2.12–1.03(m, 2H); 1.54–1.07(m, 14H); 0.9(t, 6.66 Hz, 3H)

Distribution Experiments

0.5 and 0.1 M solutions of 1,3-diols were prepared in chloroform washed with redistilled water, and then washed with a solution of I = 0.5 M with sodium chloride 0.49 M and hydrochloric acid 0.01 M. Distribution experiments were carried out at pH 2 with 1.00×10^{-2} M of boron prepared by dissolving boric acid in the aqueous phase whose ionic strength was held at 0.5 M as above. Standard boron, azomethin-H, buffer, and reagent solutions,

Table 3. Distribution data for 0.01 M boric acid in aqueous solution extracted by 0.1 M and 0.5 M 1,3-diols in chloroform and recovery values (I = 0.5 M; pH = 2; 25 ± 0.1°C).

		Distribution of $B(OH)_3$		R%	
1,3-Diols	Structure of 1,3-diols	0.1 M	0.5 M	0.1 M	0.5 M
2-Benzyl-2,4-pentanediol (**8a**)		0.057	0.448	5.45	30.93
2,4-Dimethyl-2,4-dodecanediol (**8b**)		0.084	0.360	7.71	26.49
2-Benzyl-2,4-pentanediol (**9**)		0.661	4.807	39.80	82.78
1-Benzyl-1,3-butanediol (**10a**)		1.050	7.591	51.33	88.36
2,4-Dodecanediol (**10b**)		0.167	0.507	14.33	33.65
2-Me-3-benzyl-1,3-butanediol (**11**)		3.080	20.50	75.51	95.35
2,2-DiMe-1-bnz-1,3-pr.diol (**12a**)		1.773	14.70	63.94	93.61
2,2-DiMe-1,3-undecanediol (**12b**)		0.707	2.13	41.43	68.07
1,3-Undecanediol (**13**)		0.474	2.68	32.17	72.82

conditions and equipment of distribution experiments were carried out as previously described.[27] The Azomethin-H method[28] has been used to natural solution of boron, so in this study a modified Azomethin-H method was used to determine boron because of lower pH values. Distribution data and recovery values are shown in Table 3.

RESULTS AND DISCUSSION

The dependence of classes of 1,3-diols on boron extraction has not been studied in detail. In the present study the most appropriate functional group for boron in the liquid–liquid extraction, structure based 1,3-diol, was investigated with distribution experiments. In order to nine different classes of new aliphatic 1,3-diols were synthesized by the reaction of Grignard reagents (containing octyl and benzyl as alkyl group in order to increase hydrophobicity) with different β-hydroxy carbonyl compounds which were synthesized from simple and inexpensive carbonyl compounds. Compounds **6** and **7** were protected in order to decrease the amount of Grignard reagent used but the yield of β-hydroxy protected carbonyl compounds were lower than unprotected β-hydroxy carbonyl compounds. The other experiments were carried out by excess of Grignard reagents. The yield of diols increased from 38% to 69%.

Benzyl substituted 1,3-diols with classes of 3°-3°, 2°-3°, 1°-3°, 2°-2°, 1°-2°, and octyl substituted 3°-3°, 2°-2°, 1°-2° were investigated for boron extraction capacity. The aromatic 1,3-diol structures, selectivity, their stripping facility, and the solvent effects were not investigated in the present study.

It is known that liquid–liquid extraction of boron with 1,3-diols is possible by formation of a nonionic ester complex between boric acid and aliphatic 1,3-diols in the organic phase, which are monomeric species[13] and also may be dimeric species.[29]

The following is a summary of the rules for effective extraction capacity with aliphatic 1,3-diols:

1. The total number of carbon atoms is of minor importance, because of the large dimerization constant of 1,3-diols. However, the diols with fewer than 6 carbon atoms form compounds that generally are too easily hydrolyzed or too hydrophilic, and cannot be considered for extraction use.[13]
2. The species formed between aliphatic 1,3-diols and boric acid in the organic phase must be regarded as esters; this is supported by

IR and NMR spectra. Since the two geminal methyl groups at position 2 and 3 stabilize the six-member ester ring, 2,2,4-trimethylpentanediol-1,3 (1°-3°) is thus by a the most powerful extracting reagent.[13]

3. Benzylic substitution or branched alkyl groups with up to 4 carbon atoms on the hydroxyl-bearing carbon atom and small alkyl group substitution at position 2 posses superior extraction ability or distribution ratio for boron between $CHCl_3$ and aqueous phase.
4. Both octyl and benzyl substituted 3°-3° 1,3-diols structure which investigated has the lowest extraction ability and distribution ratio for boron between $CHCl_3$ and aqueous phase. This depends probably on the steric hindrance of alkyl groups around -OH groups.
5. All of benzyl substituted 1,3-diols investigated were found to be better extractants than those octyl substituted. This selectivity depends on the formation of more stabilized complex containing six-member ring by benzyl group as a pi donor of its benzene ring.
6. Compound **11** that benzylic substitution at the OH bearing carbon and methyl substitution on second carbon of 1°-3° 1,3-diol with 12 carbon atoms possess superior extraction ability when compared with other diols investigated.
7. The order of extraction ability of 1,3-diols which substituted with benzyl group was found to be 1°-3° > 1°-2° > 2°-2° > 2°-3° > 3°-3° and substituted with octyl group, 1°-2° > 2°-2° > 3°-3° respectively.

Consequently, it is obvious that if aliphatic 1,3-diols have a carbon number limited between 8–12 and one alcohol group of them is primary (other can be tertiary or secondary), a small alkyl group such as methyl or ethyl substituted at second carbon and benzyl or branched alkyl groups with up 4 carbon substitution at 2° or 3° OH bearing carbon atom, has the best extraction capacity.

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