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Hydroboration. VII. Directive Effects in the Hydroboration of Olefins

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The hydroboration of straight-chain terminal olefins, such as 1-pentene and 1-hexene, yields products with 94% of the boron on the 1- and 6% on the 2-position of the chain. Branching of the alkyl chain, as in 3-methyl-1-butene, 3,3-dimethyl-1-butene and 4,4-dimethyl-1-pentene, does not influence the distribution appreciably. However, the phenyl substituent in styrene results in a significant change—80% primary and 20% secondary. A methyl group on the 2-carbon atom, as in 2-methyl-1-butene and 2,4,4-trimethyl-1-pentene, results in the formation of 99% of the primary derivative. Internal olefins, such as *cis*- and *trans*-2-pentene and -hexene give approximately 50–50 distribution at the two carbon atoms of the double bond, with branching immediately adjacent to the double bond resulting in a small shift of the boron atom to the more distant carbon. Thus, *trans*-*t*-butylmethylethylene results in a 42:58 distribution, with substitution favored nearer the methyl group. The marked influence of the phenyl group is shown by *trans*-phenylmethylethylene, where the boron atom prefers the position alpha to the phenyl substituent (85:15). Trimethylethylene undergoes addition to place the boron predominantly at the secondary position (98%) with only minor amounts of the tertiary derivative (2%). Similarly, 2,4,4-trimethyl-2-pentene gives 98% of the secondary derivative. Substituents in the *para* position of styrene influence the distribution of the boron atom between the α- and β-positions of the side chain: *p*-CH_3O–, 9% α; *p*-CH_3-, 18% α; *p*-H, 20% α; *p*-Cl-, 35% α. It is concluded that the direction of addition is strongly controlled by both steric and electronic influences.

The rapid, quantitative addition of diborane to olefins,[1] dienes[2] and acetylenes[3] at room temperature makes readily available a wide variety of organoboranes which are proving to be exceedingly useful in organic synthesis.[1–4] Preliminary observations indicated that the addition to an unsymmetrical olefin proceeds to place the boron atom on the less substituted of the two carbon atoms forming the double bond.[1] Since the organoborane is readily converted to the corresponding alcohol by oxidation with alkaline hydrogen peroxide, hydroboration provides a simple, convenient synthetic route for the anti-Markownikoff hydration of olefins.

The growing importance of this reaction in synthetic organic chemistry[4] suggested the desirability of a detailed, quantitative study of the direction of addition of diborane to unsymmetrical olefins. The results of this study are reported in the present publication.

Results

Numerous experiments have demonstrated that the oxidation of organoboranes by alkaline hydrogen peroxide is essentially quantitative, placing a hydroxyl group in the position previously occupied by the boron atom. Vapor phase chromatography provides a powerful analytical tool for the analysis of a mixture of isomeric alcohols. Consequently, we adopted the procedure of hydroborating the olefin at 20°, followed directly by oxidation with alkaline hydrogen peroxide. The product was treated with water, the alcohols extracted with ether, and the dried ether extract analyzed for the isomeric alcohols. In a number of representative cases, an internal standard was added to the ether extract. Yields of 90% or better were invariably indicated.

Preliminary experiments indicated that styrene differs from other simple terminal olefins in giving an organoborane with major amounts of boron on each of the two carbon atoms constituting the double bond (20% α-, 80% β-). Accordingly, this olefin was adopted to examine the influence of temperature, solvent and hydroborating agent on the direction of addition.

No significant change in the distribution was observed with lithium borohydride in ethyl ether, tetrahydrofuran or diglyme. Similar results were realized with sodium borohydride (internal generation), lithium borohydride (internal generation) or diborane (external generation), all in diglyme solution. Finally, a small increase in the amount of the α-derivative was observed with increasing temperature. These results are summarized in Table I.

TABLE I

DIRECTIVE EFFECTS IN THE HYDROBORATION OF STYRENE

Hydride source	Solvent	Temp., °C.	Product, ethanol, %[a] 1-Phenyl-	2-Phenyl-	Yield,[b] %
Lithium borohydride	Ethyl ether	20	20	80	94
	THF[c]	20	20	80	93
	Diglyme	20	21	79	94
Sodium borohydride	Diglyme	0	19	81	92
		20	20	80	94
		40	22	78	91
Diborane	Diglyme	20	18	82	95

[a] Analysis by V.P.C. on a Carbowax-20M column at 170°.
[b] Determined using benzyl alcohol as an internal standard.
[c] Tetrahydrofuran.

Since none of these variations in conditions influenced significantly the distribution of the boron atom between the α- and β-positions of the styrene molecule, we adopted for our standard hydroboration procedure the convenient addition of boron trifluoride etherate (in diglyme) to a solution of sodium borohydride and the olefin in diglyme at 20°.

In considering the effect of olefin structure on the hydroboration, it is advantageous to compare olefins with similar structural features. Consequently, the data are presented individually for olefins of the

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(1) (a) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 2582 (1956); (b) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); (c) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6423, 6428 (1959); (d) H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959).

(2) H. C. Brown and G. Zweifel, *ibid.*, **81**, 5832 (1959).

(3) H. C. Brown and G. Zweifel, *ibid.*, **81**, 1512 (1959).

(4) M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5832 (1958); J. B. Honeycutt, Jr., and J. M. Riddle, *ibid.*, **81**, 2593 (1959); W. J. Wechter, *Chemistry & Industry*, 294 (1959); R. Pappo, THIS JOURNAL, **81**, 1010 (1959); R. Dulou and Y. Chrétien-Bessière, *Bull. soc. chim. France*, **9**, 1362 (1959); S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959); S. Winstein, E. L. Allred and J. Sonnenberg, THIS JOURNAL, **81**, 5833 (1959).

following classes: I, monosubstituted terminal olefins, $RCH=CH_2$; II, disubstituted terminal olefins, $R_2C=CH_2$; III, disubstituted internal olefins, $RCH=CHR'$; IV, trisubstituted internal olefins, $R_2C=CHR$; V, p-substituted styrenes, p-XC_6H_4-$CH=CH_2$.

Monosubstituted Terminal Olefins, $RCH=CH_2$.—Simple straight-chain terminal olefins, such as 1-butene, 1-pentene and 1-hexene, give predominant addition of the boron atom to the terminal carbon atom (93–94%). Only a minor amount of addition to give the secondary alkyl boron product is observed (6–7%). These results confirm the predominant anti-Markownikoff addition reported previously.[1]

Branching of the alkyl group adjacent to the double bond does not influence the direction of addition. Thus, 3-methyl-1-butene, 3,3-dimethyl-1-butene, and 4,4-dimethyl-1-pentene give the same distribution.

As already mentioned, styrene gives 80% addition of the boron to the terminal position, 20% to the secondary carbon. Finally, the influence of the phenyl group is diminished, but still evident in allylbenzene, with a 90:10 distribution. These results are summarized in Table II.

TABLE II

DIRECTIVE EFFECTS IN THE HYDROBORATION OF MONOSUBSTITUTED TERMINAL OLEFINS, $RCH=CH_2$ AT 20°

Olefin	Alcohol product, %	
	1-ol	2-ol
1-Butene	93	7
1-Pentene	94	6
1-Hexene	94	6
3-Methyl-1-butene	94	6
3,3-Dimethyl-1-butene	94	6
4,4-Dimethyl-1-pentene	93	7
Styrene	80	20
Allylbenzene	90	10

Disubstituted Terminal Olefins, $R_2C=CH_2$.—In the case of disubstituted terminal olefins, the directive effect of the two substituents is overwhelming and results in the almost complete addition of the boron atom to the terminal carbon. Thus 2-methyl-1-butene gives 99% of the primary alkylborane with only 1% of the tertiary derivative. Similar results are observed with 2,4,4-trimethyl-1-pentene and α-methylstyrene (Table III).

TABLE III

DIRECTIVE EFFECTS IN THE HYDROBORATION OF DISUBSTITUTED TERMINAL OLEFINS, $R_2C=CH_2$, AT 20°

Olefin	Alcohol product, %	
	1-ol	2-ol
2-Methyl-1-butene	99	1
2,4,4-Trimethyl-1-pentene	99	1
α-Methylstyrene	100	Trace

Disubstituted Internal Olefins, $RCH=CHR'$.—2-Pentene and 2-hexene undergo addition to place the boron in approximately equal amounts on the 2- and 3-carbon atoms. Only minor variations in the distribution are observed for the individual *cis* and *trans* isomers. Branching of one of the two alkyl groups attached to the double bond, as in *trans*-4-methyl-2-pentene and *trans*-4,4-dimethyl-2-pentene, results in a small preference of the boron atom for the carbon atom adjacent to the less branched of the alkyl substituents. It is of interest that in the case of *trans*-4,4-dimethyl-2-pentene the reaction proceeds only to the dialkylborane stage.

Comparison of the behavior of 1-pentene and styrene (Table II) indicates that the phenyl group is less effective than the alkyl group in directing the boron atom to the terminal carbon. The same relative effect of the phenyl and methyl groups is indicated by the distribution observed for *trans*-1-phenylpropene-85% α- and 15% β-. These results are summarized in Table IV.

TABLE IV

DIRECTIVE EFFECTS IN THE HYDROBORATION OF DISUBSTITUTED INTERNAL OLEFINS, $RCH=CHR'$ AT 20°

Olefin	Alcohol product, %	
	2-ol	3-ol
cis-2-Pentene	55	45
trans-2-Pentene	51	49
cis-2-Hexene	50	50
trans-2-Hexene	46	54
cis-3-Hexene		100
trans-4-Methyl-2-pentene	57	43
trans-4,4-Dimethyl-2-pentene[a]	58	42
trans-1-Phenylpropene	85[b]	15[c]

[a] Hydroboration to R_2BH stage only. [b] 1-Phenyl-1-propanol. [c] 1-Phenyl-2-propanol.

Trisubstituted Olefins, $R_2C=CHR$.—2-Methyl-2-butene undergoes hydroboration to give 98% of the secondary derivative, with only 2% of the tertiary compound. In the case of 2,4,4-trimethyl-2-pentene, the distribution of the boron between the secondary and tertiary positions is the same. In both cases, hydroboration under mild conditions proceeds only to the dialkylborane stage.[1]

In an earlier study of the hydroboration of 2,4,4-trimethyl-2-pentene, the formation of both secondary and tertiary alcohol was observed and reported.[1c] Fractionations did not yield a clean separation, so that no analysis was reported. We now believe that the formation of the tertiary alcohol was the result of a partial isomerization of the initial product, bis-2,4,4-trimethyl-2-pentylborane, which undergoes isomerization under exceedingly mild conditions.[5] These results are summarized in Table V.

TABLE V

DIRECTIVE EFFECTS IN THE HYDROBORATION OF TRISUBSTITUTED OLEFINS, $R_2C=CHR$, AT 20°

Olefin	Alcohol product, %	
	Secondary	Tertiary
2-Methyl-2-butene[c]	98[a]	2
2,4,4-Trimethyl-2-pentene[c]	98[b]	2

[a] 3-Methyl-2-butanol. [b] 2,4,4-Trimethyl-3-pentanol. [c] Hydroboration to R_2BH stage only.

***p*-Substituted Styrenes.**—The marked influence of the phenyl group in styrene on the direction of addition of diborane to the double bond made it of interest to examine a number of representative *para* substituted styrenes. It was hoped that the influence of the substitutent might prove of assistance in understanding the nature of the forces controlling the direction of the addition reaction.

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(5) Research in progress.

A *p*-methyl substituent exerted only a minor effect, decreasing the amount of alpha-substitution to 18% from the 20% observed for styrene itself. The *p*-methoxy group exhibited a far more powerful effect, decreasing the amount of *alpha* substitution to 9%. Finally the *p*-chloro substituent increases the yield of *alpha* product to 35%. These results are summarized in Table VI.

TABLE VI

DIRECTIVE EFFECTS IN THE HYDROBORATION OF *p*-SUBSTITUTED STYRENES, *p*-$XC_6H_4CH{=}CH_2$, AT 20°

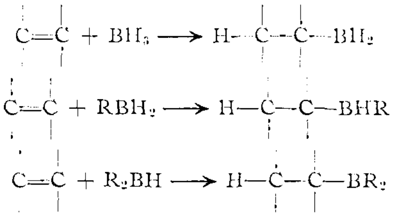
Olefin	—Alcohol product, %—	
	α-ol	β-ol
p-Methoxystyrene	9	91
p-Methylstyrene	18	82
Styrene	20	80
p-Chlorostyrene	35	65

Discussion

Diborane exists as a dimer in the gaseous state, but dissociates to a greater or lesser degree to monomeric borane etherates in various ether solvents.[6,7] Presumably the marked catalytic effect of ether solvents upon the addition reaction is attributable to their ability to dissociate the diborane molecule. In the absence of any information as to the precise state of diborane and the intermediate alkylated diboranes in the ether solvents, it is convenient to discuss the reaction in terms of the simple monomeric species, borane.

The observation that the change in the ether solvent from ethyl ether to tetrahydrofuran to diglyme does not influence significantly the isomer distribution in the hydroboration of styrene (Table I) suggests that the ether is not intimately involved in the transition state controlling the direction of addition. It is also of interest that there is no significant difference in the direction of addition as the hydroborating agent is varied from lithium borohydride to sodium borohydride to diborane itself. Finally, the small influence of temperature upon the isomer distribution suggests that the energy of activation for the hydroboration reaction must be quite small, with only minor differences for the two reaction paths leading to the two possible hydroboration products.

The addition of diborane to olefins must involve at least three distinct stages, in which one, two and three carbon–boron bonds are formed (1–3).



$$\mathrm{C{=}C + BH_3 \longrightarrow H{-}C{-}C{-}BH_2} \qquad (1)$$

$$\mathrm{C{=}C + RBH_2 \longrightarrow H{-}C{-}C{-}BHR} \qquad (2)$$

$$\mathrm{C{=}C + R_2BH \longrightarrow H{-}C{-}C{-}BR_2} \qquad (3)$$

In this study we established the direction of addition by oxidizing the final product to the corresponding alcohols. Clearly, the final isomer distribution is the result of three successive stages, and there is no assurance that the distribution of the boron between the two available carbon atoms of the double bond is the same in each stage. Indeed, we have evidence that the distribution can vary with successive substitution of the borane group.

Fortunately, this does not constitute a major problem in considering the present results. In the great majority of cases the addition occurs predominantly in one direction. With yields of 94 to 98% of a single isomer realized, it is apparent that the direction of addition cannot vary greatly in the individual stages of these particular reactions. Only in the case of additions to styrene (20% α) and *p*-chlorostyrene (35% α) is there uncertainty as to whether the boron atom prefers the α- or β-carbon atom in the initial stage of the addition reaction.

With the great majority of olefins, the reaction proceeds to the trialkylborane stage, R_3B. With relatively hindered olefins, such as 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, the reaction at room temperature proceeds only to the dialkylborane stage, R_2BH. Finally, with 2,3-dimethyl-2-butene, the reaction ceases at the monoalkylborane stage, RBH_2.

The same phenomenon is now apparent with simple dialkylethylenes containing bulky *t*-butyl groups. Thus, the hydroboration of *trans*-2-pentene proceeds to the R_3B stage, that of *trans*-methyl-*t*-butylethylene to the R_2BH stage, and that of *trans*-di-*t*-butylethylene stops at the RBH_2 stage.[8]

These results clearly point to the importance of steric effects in controlling the extent of reaction between a given olefin and diborane.

That steric effects also play a role in controlling the direction of addition of diborane to the double bond is indicated by our results with bis-3-methyl-2-butylborane, R_2BH, formed in the reaction of diborane with 2-methyl-2-butene. Whereas the reaction of diborane with 1-hexene yields 6% of the secondary alkyl boron derivative, the hindered dialkylborane yields a product with 1-hexene which contains no more than 1% of the boron at the secondary position.[9]

It is therefore tempting to ascribe the predominant addition of the double bond to the operation of steric effects.

It would be possible on this basis to account for the high preference of the boron atom for the terminal carbon atom of monoalkylethylenes, $RCH{=}CH_2$ (94%), the terminal atom of 1,1-dialkylethylenes, $R_2C{=}CH_2$ (99%), and the secondary carbon atom of trialkylethylenes, $R_2C{=}CHR$ (98%).

However, our data clearly indicate that steric effects cannot be the complete answer. No significant change in the direction of addition is observed for ethylethylene (93% 1-), isopropylethylene (94% 1-), *t*-butylethylene (94% 1-), or neopentylethylene (93% 1-). Moreover, the shifts in distribution observed for $RCH{=}CHCH_3$ (51% 2- for R = ethyl; 57% 2- for R = isopropyl;

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[6] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

[7] J. R. Elliott, W. L. Roth, G. F. Roedel and E. M. Boldebuck, *ibid.*, **74**, 5211 (1952); B. Rice, J. A. Livasy and G. W. Schaeffer, *ibid.*, **77**, 2750 (1955); B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955).

[8] T. J. Logan and T. J. Flautt, THIS JOURNAL, **82**, 3446 (1960).

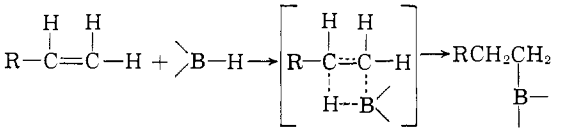
[9] A detailed study of the additon of the hindered borane to a number of representative olefins is under study by Dr. George Zweifel and will be reported shortly.

58% 2- for R = *t*-butyl[10]), although in the direction to be predicted for steric control, appear far too small to account for the major directive effects observed in the terminal and trisubstituted olefins. Finally, the relatively large amount of addition to the α-position of styrene is also not explicable in terms of steric influence alone.

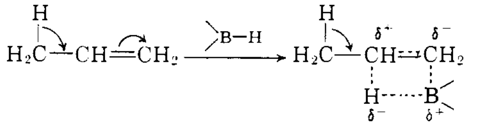
Similar results have been observed in the addition of diethylaluminum hydride to 1-hexene[11] and to styrene.[12] The 1-hexene adds the aluminum–hydrogen bond to place the aluminum practically exclusively on the terminal carbon, whereas in the case of styrene 22–24% of the aluminum becomes attached to the α-carbon atom of the side chain.[13]

The available data clearly require that electronic influences play an important role in controlling the direction of addition of the boron–hydrogen bond to the double bond. This conclusion is confirmed by the marked influence exerted by *para* substituents in the styrene molecule on the direction of addition (Table VI).

The addition of diborane to cyclic olefins[1d] and to acetylenes[3] occurs cleanly *cis*. Consequently, it appears that the addition must involve a four-center transition state (4).

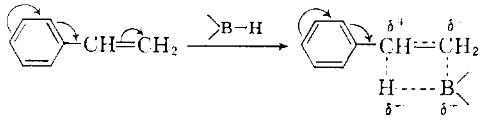

(4)

The boron-hydrogen bond is presumably polarized, with the hydrogen having some hydridic character. Consequently, the electronic shifts generally used to account for the normal addition of hydrogen chloride to propylene[14] can be applied to account for the preferred addition of the boron atom to the terminal position (5).

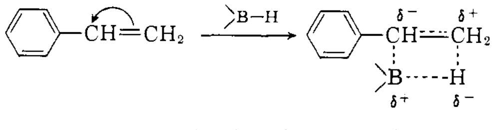

(5)

The same explanation can be extended to account for the enhanced preference of boron for the terminal carbon atom of the 2,2-dialkylethylenes (99% 1-), as well as for the preferred substitution (98%) in the secondary position of the trisubstituted olefins.

In the case of styrene, similar arguments can be used to account for the observed preference of the boron atom for the terminal position (6).


(6)

In order to account for the enhanced substitution which occurs in the α-position, we must recognize that the phenyl group can also stabilize a negative charge in the α-position, as in the benzyl anion (7).[14] This transition state would be stabilized


(7)

by an electron-withdrawing substituent, such as *p*-chloro-, and rendered less stable by an electron-supplying substituent, such as *p*-methoxy.

A similar influence of the phenyl substituent appears to persist to a small degree in allylbenzene, which exhibits a 90:10 distribution between the primary and secondary positions. It is also noteworthy that in *trans*-phenylmethylethylene, where the effect of the two groups are directly competitive, there is observed 85% substitution alpha to the phenyl group.[15] Finally, it should be pointed out that in 1,1-diphenylethylene, addition of the boron occurs predominantly to the terminal position.[1a] Evidently, the combined steric effect of the two phenyl groups overcomes their tendency to direct boron toward the α-position.

Finally, we should call attention to the interesting observation by D. Seyferth that trimethylvinylsilane undergoes hydroboration to place 37% of the boron in the secondary position[16] as compared with 6% addition in the analogous position for *t*-butylethylene. This observation suggests that functional substituents on the double bond may greatly influence the direction of addition, and we are undertaking a detailed study of this possibility.[17]

Experimental Part

Materials.—Ethyl ether, tetrahydrofuran and diglyme were purified as described in earlier papers.[1] In all cases the solvents were given a final distillation from lithium aluminum hydride, the distillation being under vacuum for diglyme. Boron trifluoride etherate was purified by distillation under vacuum. Sodium borohydride and lithium borohydride (Metal Hydrides Inc.) were used without further purification.

The source of the olefins used, their specified purities, and refractive index values are summarized in Table VII.

In the great majority of cases, the alcohol products were identified by comparison in the V.P.C. apparatus with authentic samples of the two isomeric alcohols. In a few cases we were content to identify one of the two peaks, and in two cases (3,3-dimethyl-1-butene and α-methylstyrene) we were content to base our assignment of the peaks on the previously established structure of the alcohols produced *via* the hydroboration procedure.[1a] In Table VII are also summarized the alcohols used as references and the columns and temperature used for the V.P.C. analyses.

Hydroboration Procedure.—In a dry three-neck flask, equipped with a condenser, a thermometer and a pressure-equilibrated dropping funnel were placed 50 mmoles of the olefin and 28 ml. of a 0.5 molar solution of sodium borohydride in diglyme. The flask was immersed in a water-bath at 20°. Boron trifluoride etherate, 18.8 mmoles, diluted with 5.0 ml. of diglyme was added over a period of 30 minutes to the well-stirred reaction mixture. After an additional hour at 20°, the flask was immersed in an ice-bath, 5 ml. of water

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(10) In the latter case the reaction stops at the R_2BH stage. It is probable that for R = isopropyl, the corresponding value for the distribution at the R_2BH stage would be somewhat smaller than the 57% value given above for the complete reaction.

(11) K. Ziegler, H. G. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 91 (1954).

(12) G. Natta, P. Pino, G. Mazzanti, P. Longi and F. Bernardini, THIS JOURNAL, **81**, 2561 (1959).

(13) It is of interest to note that the addition of diethylaluminum hydride to styrene was accomplished in 17 hours at 100°, whereas the addition of diborane to styrene was complete within minutes at room temperature.

(14) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 430–442.

(15) In *p*-anisylmethylethylene hydroboration places 75% of the boron alpha to the aromatic ring; S. Winstein, E. L. Allred and J. Sonnenberg, THIS JOURNAL, **81**, 5833 (1959). This decrease in product containing the boron alpha to the *p*-anisyl group is similar to the decreased addition in the α-position observed for *p*-methoxystyrene.

(16) D. Seyferth, *J. Inorg. Nucl. Chem.*, **7**, 152 (1958).

(17) Work in progress with Mr. K. Keblys.

TABLE VII

SUMMARY OF DATA FOR THE OLEFINS USED AND THE V.P.C. ANALYTICAL DATA

Olefin	Source	Purity	n^{20}_{D}	n^{20}_{D} (lit.)	Reference alcohols	Column	Temp., °C.
1-Butene	Phillips[a]	99			1-, 2-Butanol[e]	Diglycerol	70
1-Pentene	Phillips	99			1-,[e] 2-Pentanol[f]	Diglycerol	70
1-Hexene	Phillips	99	1.3880	1.3878	1-, 2-Hexanol[e,f]	D + GAC[j]	90
3-Methyl-1-butene	Phillips	99			3-Methyl-1-butanol[e] 3-Methyl-2-butanol[e]	Glycerol	70
3,3-Dimethyl-1-butene	API[b]	99.8				Diglycerol	80
4,4-Dimethyl-1-pentene	API	99.8				Diglycerol	90
Styrene	Matheson		1.5468	1.5433 (25°)	1-Phenyl-1-ethanol[g] 2-Phenyl-1-ethanol[e]	Carbowax-20M	170
Allylbenzene	API	99	1.5115	1.5110 (22°)	1-Phenyl-2-propanol[e] 3-Phenyl-1-propanol[e]	Carbowax-20M	170
2-Methyl-1-butene	Phillips	99	1.3797	1.3778	2-Methyl-1-butanol[e] 2-Methyl-2-butanol[e]	Glycerol	70
2,4,4-Trimethyl-1-pentene	Phillips	99	1.4093	1.4086	2,4,4-Trimethyl-1-[h] 2,4,4-Trimethyl-2-pentanol[i]	Carbowax-1500	100
α-Methylstyrene	Dist. prod.	99.5	1.5385	1.5384 (17°)		Carbowax-20M	170
cis-2-Pentene	Synthesized[d]				2-, 3-Pentanol[f]	Diglycerol	70
trans-2-Pentene	API	98			2-, 3-Pentanol[f]	Diglycerol	70
cis-2-Hexene	API	99			2-, 3-Hexanol[f]	Diglycerol	90
trans-2-Hexene	API	98.5	1.3938	1.3935	2-, 3-Hexanol[f]	Diglycerol	90
cis-3-Hexene	Synthesized[d]		1.3955	1.3947	3-Hexanol[f]	Diglycerol	90
trans-4-Methyl-2-pentene	Phillips	99.8	1.3891	1.3889	4-Methyl-2-pentanol[f]	Diglycerol	90
trans-4,4-Dimethyl-2-pentene	API	98	1.3984	1.3982	4,4-Dimethyl-2-pentanol[f]	Diglycerol	90
trans-1-Phenylpropene	API	99.8			1-Phenyl-1-propanol[e] 1-Phenyl-2-propanol[e]	Carbowax-20M	170
2-Methyl-2-butene	Phillips	99	1.3890	1.3872	2-Methyl-2-butanol[e] 3-Methyl-2-butanol[e]	Glycerol	70
2,4,4-Trimethyl-2-pentene	Phillips	95	1.4093	1.4086	2,4,4-Trimethyl-2-[i] 2,4,4-trimethyl-3-pentanol[f]	Carbowax-1500	100
p-Methoxystyrene	Monomer[c]		1.5601	1.5595 (23°)	1-*p*-Anisyl-1-ethanol[g]	Carbowax-1500	190
p-Methylstyrene	Monomer[c]		1.5423	1.5395 (26°)	1-*p*-Tolyl-1-ethanol[g]	Carbowax-20M	190
p-Chlorostyrene	Monomer[c]		1.5631	1.5650	1-*p*-Chlorophenyl-1[g] ethanol	Carbowax-20M	190

[a] Phillips Petroleum Co. [b] American Petroleum Project No. 45 at Ohio State University. [c] Monomer–Polymer Corp. [d] Ref. 3. [e] Commercial laboratory chemical. [f] Synthesized *via* Grignard. [g] Synthesized by reduction of ketone. [h] Synthesized by hydroboration. [i] Synthesized by hydrolysis of tertiary chloride; H. C. Brown and H. L. Berneis, THIS JOURNAL, **75,** 10 (1953). [j] One-meter column of diglycerol, followed by 1-meter column of glycerol–acrylonitrile adduct (to separate diglyme from 1-hexanol).

was added to destroy residual hydride, and the reaction mixture was oxidized by adding slowly 5.3 ml. of 30% hydrogen peroxide, adding sufficient alkali to maintain the solution slightly alkaline (*p*H 8). The solution was poured into water and the alcohols formed were extracted with ether (3 × 50 ml.). The combined ether extracts were washed with a small quantity of saturated sodium bicarbonate solution, the ether layer separated, and dried over anhydrous magnesium sulfate.

The solution was analyzed by V.P.C. (Perkin–Elmer chromatograph with a Brown 1 mv. recorder fitted with a Disc Integrator), comparing the peaks with those of authentic samples. These samples were: (1) commercial products, (2) synthesized *via* the Grignard reaction, (3) synthesized by reduction of the ketones or (4) samples available from earlier work on the hydroboration of olefins. Since all are well known, well characterized compounds, details of their preparation and purification are not included. In a number of cases we prepared synthetic mixtures and established that we could reproduce their composition to ±1%.

In a representative number of cases, 50 mmoles of reference alcohol was added to the ether solution and the yields determined. Yields of 90–95% were realized (Table I).

In the case of two olefins, 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, the reaction proceeds only to the dialkylborane stage.[1b] In these cases we increased the amount of sodium borohydride and boron trifluoride etherate by 50%, maintaining the remainder of the procedure constant.

In the case of 4,4-dimethyl-2-pentene we used the usual hydroboration procedure, but observed at the end of the reaction the liberation of 16 mmoles of hydrogen in excess of the usual small amount; V.P.C. examination of the reaction mixture revealed the presence of 12 mmoles of unreacted olefin. Consequently, it is clear that in this case the reaction proceeds rapidly to the dialkylborane stage, and only slowly beyond that stage.

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