at δ 7.34 and 7.26, characteristic of amide NH_2 protons, and the doublet at high field, 2.93, due to one of the 5′ protons. Contrarily, II displays both 5′ doublets at low field and no exchangeable NH_2 protons. The closely spaced singlets of the purine base protons are arbitrarily assigned with H_8 at lowest field in the spectrum of II.

Natural abundance cmr measurements are even more revealing. The decoupled spectrum of II has one resonance, C_6, in the carbonyl region of inosine at −36.3 ppm.[7] On the other hand, the decoupled spectrum of I contains two peaks superimposed at −35.7 ppm, indicating two carbonyl carbons, C_6 and C_2. In addition, the loss of the conjugated purine ring is noticed in the upfield shift of C_5, from 71.3 in II to 82.6 ppm in I.

Perhaps the most succinct structural information is derived from the undecoupled cmr spectra. The vicinal $^3J_{C_6-H_2}$ of the usual magnitude (∼9–12 Hz[8-10]) is observed in II, but is completely absent in I, indicative of no bond between N_1 and C_2.

This report illustrates the utility of cmr in nucleoside structural analysis.

Acknowledgment.—We thank Mr. E. B. Banta for expert technical assistance and Dr. R. Rousseau for helpful discussions.

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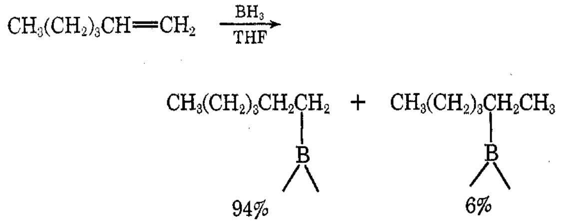
Received October 12, 1972

An Unusually Powerful Directive Effect in the Hydroboration of Representative Olefins with Monochloroborane–Ethyl Etherate

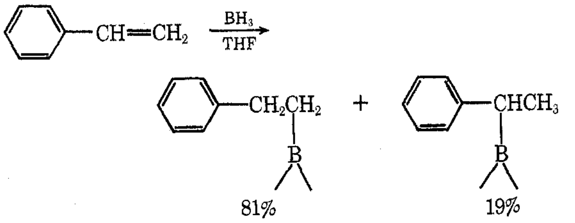
Summary: Hydroboration–oxidation of alkenes with monochloroborane (BH_2Cl) in ethyl ether gives the anti-Markovnikov alcohols in >99.5% isomeric purity, revealing a directive effect in the addition stage far stronger than that exhibited by borane–tetrahydrofuranate itself.

Sir: The hydroboration of representative olefins with monochloroborane–ethyl etherate ($BH_2Cl–OEt_2$) reveals a powerful directive effect which greatly reduces the yield of the minor isomer formed in hydroborations with borane itself. Consequently, hydroboration with monochloroborane (BH_2Cl) makes possible the synthesis of the major product in purities which often exceed 99.5%.

A difficulty in using hydroboration–oxidation for the anti-Markovnikov hydration of olefins[1] is the formation of significant amounts of the minor isomer in the hydroboration stage (eq 1 and 2). This phenomenon often makes necessary a tedious purification to remove the minor component. Hydroboration with disiamylborane has been recommended as a means of overcoming this difficulty. However, the reagent hydroborates internal and cyclic olefins only very sluggishly.[2] Moreover, here also it is necessary to separate the desired product from the *sec*-isoamyl alcohol resulting from the oxidation of the disiamylborane moiety. We wish to report here a new more readily and generally applied procedure to avoid these difficulties.

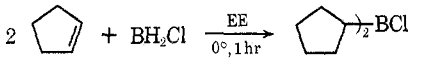


(1)



(2)

We recently discovered that monochloroborane in ethyl ether (EE) in contrast to monochloroborane in tetrahydrofuran (THF) readily hydroborates a wide variety of olefins to give the corresponding dialkylchloroboranes[3] (eq 3). The reaction in THF proceeds to give a mixture of products, R_3B, R_2BCl, and $RBCl_2$.[3]



(3)

It has been reported that in THF chloroborane had little, if any, advantage over BH_3 in the directive effects achieved. Thus Zweifel found that the hydroboration–oxidation of 1-hexene gave 94% 1-hexanol with 6% 2-hexanol.[4] Similarly, Pasto and Balasubramaniyan observed a 96:4 distribution of the two products.[5]

We discovered that hydroboration with BH_2Cl in ethyl ether exhibits a far more powerful directive effect. Thus 1-hexene yields >99.5% 1-hexanol with <0.5% 2-hexanol. Styrene (eq 2) gives 96% primary derivative with 4% secondary. Norbornene gives >99.8% exo alcohol. 1-Methylcyclopentene gives >99.8% the *trans*-2-methylcyclopentanol, with no cis isomer and only <0.2% tertiary isomer indicated.

The following procedure for the hydroboration–oxidation of 1-methylcyclopentene with $BH_2Cl–OEt_2$ is representative. In a dry 50-ml flask under nitrogen was taken 5 mmol of BH_2Cl in ethyl ether[6] (3.7 ml)

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[1] (a) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **82**, 4708 (1960); (b) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962; (c) H. C. Brown and R. L. Sharp, *J. Amer. Chem. Soc.*, **88**, 5851 (1966).

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[3] H. C. Brown and N. Ravindran, *ibid.*, **94**, 2112 (1972).

[4] G. Zweifel, *Organometal. Chem.*, **9**, 215 (1967).

[5] D. J. Pasto and P. Balasubramaniyan, *J. Amer. Chem. Soc.*, **89**, 295 (1967).

[6] The BH_2Cl solution in ethyl ether was prepared by adding stoichiometric quantity of $LiBH_4$ in ethyl ether solution to a solution of BCl_3 in ethyl ether at 0°, according to eq i.

$$LiBH_4 + BCl_3 + 2Et_2O \xrightarrow{EE} LiCl + 2BH_2Cl–OEt_2 \qquad (i)$$

at 0°. The hydroboration was done by adding 10 mmol of 1-methylcyclopentene and stirring for 2 hr at 0°. For the oxidation 15 ml of ethanol was added, followed by 5 ml of ~3 *N* NaOH, and 2 ml of 30% H_2O_2 added dropwise (vigorous reaction). The completion of the oxidation was ensured by maintaining the reaction mixture at 50° for 15 min. The absolute and relative yields of the alcohols were determined by glpc using undecane as the internal standard. (The amount of the internal standard was chosen such that its peak size was closer to that of the minor component. The reliability of the instrument in determining the minor component present in such small quantities was checked by analyzing known synthetic mixtures of the two components in the proportions expected from the reaction.) *trans*-2-Methylcyclopentanol were obtained in 94% yield. There was present <0.2% tertiary alcohol and no cis isomer.

The results are summarized in Table I together with comparable data for hydroboration with BH_3 in THF.

TABLE I

PRODUCTS FROM HYDROBORATION–OXIDATION OF REPRESENTATIVE OLEFINS WITH BH_2Cl IN ETHYL ETHER AND BH_3 IN TETRAHYDROFURAN

Olefin	Products	Relative yield of products, %	
		BH_2Cl–OEt_2[a]	BH_3–THF[b]
1-Hexene	1-Hexanol	>99.5	94
	2-Hexanol	<0.5	6
2-Methyl-1-butene	2-Methyl-1-butanol	>99.9	99
	2-Methyl-2-butanol	<0.1	1
Norbornene	*exo*-2-Norbornanol	>99.8	99
	endo-2-Norbornanol	<0.2	1
2-Methyl-2-butene	3-Methyl-2-butanol	99.7	98
	2-Methyl-2-butanol	0.3	2
1-Methylcyclopentene	*trans*-2-Methylcyclopentanol	>99.8	98.5
	1-Methylcyclopentanol	<0.2	1.5
Styrene	2-Phenylethanol	96	81[c]
	1-Phenylethanol	4	19[c]
α-Methylstyrene	2-Phenyl-1-propanol	100	100
	2-Phenyl-2-propanol	0	0
2-Pentene	2-Pentanol	58[d]	55[d]
	3-Pentanol	41[d]	45[d]
4-Methyl-2-pentene	4-Methyl-2-pentanol	60[d]	57[e]
	2-Methyl-3-pentanol	40[d]	43[e]
4,4-Dimethyl-2-pentene	4,4-Dimethyl-2-pentanol	79[d]	58[e]
	2,2-Dimethyl-3-pentanol	21[d]	42[e]

[a] Total yields were 95 ± 5%. [b] Reference 1a,b. [c] Reference 1c. [d] Cis olefin. [e] Trans olefin.

The results with olefins, such as 2-pentene, 4-methyl-2-pentene, and 4,4-dimethyl-2-pentene, reveal a slightly greater directive effect compared to BH_3, but very minor compared to disiamylborane. Consequently, disiamylborane remains the hydroborating agent of choice when it is desirable to use steric effects to control the direction of addition. The results with the 2-pentenes show that the direction of addition of BH_2Cl is not significantly influenced by steric effects. Therefore, the powerful directive effects observed with the other olefins must be due to electronic (polar) effects.

The question arises as to why the results for the directive effects are so different in ethyl ether from those reported for THF. The reaction in THF is relatively slow. In fact, it may be that only a small part of the reaction in THF proceeds through the monochloroborane–tetrahydrofuranate, but proceeds instead through a small equilibrium concentration of borane (eq 4). ($BHCl_2$ in THF does not hydroborate

$$2ClH_2B\text{–}THF \rightleftharpoons Cl_2HB\text{–}THF + H_3B\text{–}THF \qquad (4)$$

olefins to any significant extent under these conditions[7].) On the other hand, there is little doubt that the hydroboration in ethyl ether must be proceeding through the BH_2Cl entity.

In any case, it is quite clear that hydoboration with monochloroborane–ethyl etherate not only provides a convenient route to dialkylchloroboranes and the corresponding borinic acids and esters, but also provides the anti-Markovnikov alkylborane moiety in far higher isomeric purity than hydroboration with borane itself. This development greatly extends the utility of the hydroboration reaction for the synthesis of regiospecifically and stereochemically pure derivatives.

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[7] H. C. Brown and N. Ravindran, unpublished results.

[8] Postdoctoral research associate on National Science Foundation Grant No. 27742X.

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RECEIVED OCTOBER 11, 1972

Migrations in Oxidations of Trisubstituted Anilines

Summary: Homogeneous oxidations of mesidine in moderately acidic mixtures containing methanol afford the expected azo compound and two anils, one of which, 2,6-dimethyl-3-methoxymethyl-*p*-benzoquinone 4-(2′,4′,6′-trimethyl)anil, is formed by an alkyl shift.

Sir: The peroxidase-catalyzed oxidative dealkylation of mesidine (**1**) to the quinone anil **3**, was disclosed by Chapman and Saunders in 1941.[1] Subsequently the reaction was repeated with a variety of chemical oxidants.[2] We wish to report that mesidine can be transformed by several oxidizing systems into an anil, **4**, containing a shifted alkyl group. We consider this finding to be the first case of an alkyl shift in a nonenzymatic oxidation of a substituted aniline. Saunders and colleagues[3] have invoked an alkyl shift in the peroxidase oxidation of 2,4-dimethylaniline[4] to explain the formation of a minor product.

Mesidine, **1**, was oxidized by ferricyanide in a methanol–water mixture to give azo **2**, anil **3**, and a new anil **4** [2,6-dimethyl-3-methoxymethyl-*p*-benzoquinone-4-(2′,4′,6′-trimethyl)anil]. The respective yields were 1.5, 54, and 17%, when a reaction mixture of 0.010 mol of mesidine and 0.076 mol of potassium

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(4) The shifted product, 2,5-dimethyl-*p*-benzoquinone bis(2,4-dimethyl)-anil, was formed in 3% yield.