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Hydroboration Kinetics. 13. Kinetics and Mechanism of Hydroboration of Representative Alkenes and Alkynes with Dibromoborane–Methyl Sulfide. Remarkable Catalysis of the Reaction by Small Quantities of Boron Tribromide[1]

Herbert C. Brown* and J. Chandrasekharan[2]

R. B. Wetherill and H. C. Brown Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907

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The rate of hydroboration of 1-hexene with dibromoborane–methyl sulfide, $BHBr_2{\cdot}SMe_2$, followed by monitoring the B–H stretching absorption of the reagent at 2500 cm^{-1} by the quantitative IR procedure at 25 °C in CH_2Cl_2 is retarded by the product of the reaction, $RBBr_2{\cdot}SMe_2$. Added methyl sulfide, Me_2S, represses the rate even more severely. These facts strongly suggest that the mechanism involves a prior dissociation of the reagent into $BHBr_2$ and Me_2S, followed by the reaction of $BHBr_2$ with the alkene to give $RBBr_2$; $RBBr_2$ complexes with the Me_2S formed in the dissociation step to give the observed product. The rate retardation by the product arises from the fact that it is a less stable complex than $BHBr_2{\cdot}SMe_2$ and consequently provides a small concentration of Me_2S. As expected for this mechanism, the reaction of 1-hexene with $BHBr_2{\cdot}SMe_2$ under stoichiometric conditions (0.100 M each) displays complex kinetics. However, in the presence of added Me_2S (1 equiv), good second-order kinetics is observed. The pseudo-second-order rate constant shows a linear dependence on the concentration of Me_2S. The ratio of the pseudo-second-order rate constants of a given pair of alkenes is essentially identical at several different concentrations of Me_2S, showing that the selectivity of $BHBr_2{\cdot}SMe_2$ is independent of added Me_2S in conformity with the proposed mechanism. The kinetics were also followed for a number of alkenes and alkynes in the presence of added Me_2S at 25 °C in CH_2Cl_2. In all cases studied, clean second-order rate behavior was realized. The ratios of the pseudo-second-order rate constants are in reasonable agreement with the relative reactivities established earlier by the competition method, thus providing a quantitative picture of the effect of structure on the reactivity of these compounds toward $BHBr_2{\cdot}SMe_2$. In conformity with the dissociation mechanism, hydroboration by $BHBr_2{\cdot}SMe_2$ is remarkably catalyzed by small quantities of BBr_3, incidentally offering a convenient method to achieve the hydroboration of even sluggish alkenes, such as cyclohexene, with ease. The dissociation mechanism also explains why $BHBr_2{\cdot}SMe_2$, despite its greater stability and lower dissociation, is a more powerful hydroborating agent than $BHCl_2{\cdot}SMe_2$, with its lower stability and higher dissociation.

In recent years dibromoborane–methyl sulfide,[3] $BHBr_2{\cdot}SMe_2$, has found extensive use in organic synthesis.[4] However, the mechanism of its reaction with alkenes is not yet fully understood. A proper understanding of the mechanism of this reaction will be useful not only to develop the chemistry of haloborane reagents, but also to provide an insight into the mechanism of hydroboration with borane–Lewis base complexes in general.

Recently we established that hydroboration of alkenes with 9-BBN·Lewis base complexes proceed by the dissociation mechanism.[5] For example, excess Me_3N represses the rate of hydroboration of 2-methyl-1-pentene by 9-BBN·NMe_3 complex significantly, indicating that the complex dissociates into 9-BBN and Me_3N prior to hydroboration. Our studies on BH_3·Lewis base complexes indicated that the rate of hydroboration increases with decreasing stability of the complex and that it is repressed by excess ligand.[6,7] Moreover, we studied the kinetics of hydroboration of 2,3-dimethyl-2-butene with $BH_3{\cdot}SMe_2$ and showed that the reaction proceeds by a dissociation mechanism as well.[7] Consequently, by extrapolation, it is possible that the behavior of haloborane–methyl sulfide complexes would be similar. In fact our early studies showed that the hydroboration of alkenes and alkynes with $BHBr_2{\cdot}SMe_2$ and *tert*-hexylchloroborane–methyl sulfide is significantly retarded by the addition of Me_2S (1 equiv).[8,9]

Unfortunately, we encountered an unexpected theoretical problem. $BHBr_2{\cdot}SMe_2$ hydroborates alkenes much faster than does $BHCl_2{\cdot}SMe_2$.[10] Since BBr_3 is a stronger Lewis acid than BCl_3,[11] $BHBr_2$ should be a stronger acid than $BHCl_2$. This would make $BHBr_2{\cdot}SMe_2$ a tighter complex than $BHCl_2{\cdot}SMe_2$. Consequently, according to the dissociation mechanism, one would expect $BHCl_2{\cdot}SMe_2$ to hydroborate alkenes faster than $BHBr_2{\cdot}SMe_2$. In practice, however, the hydroboration of alkenes by $BHCl_2{\cdot}SMe_2$ is much slower, and 1 molar equiv of BCl_3 is needed to effect a satisfactory hydroboration.[10] Moreover, at the time of exploration of $BHBr_2{\cdot}SMe_2$ as a hydroborating agent, we had observed that the hydroboration of 2-methyl-2-butene with $BHBr_2{\cdot}SMe_2$ led to 7% of boron on the *tertiary* carbon, much higher than that observed for either $BHCl_2{\cdot}SMe_2$ or $BHI_2{\cdot}SMe_2$ (3%).[10] These observations led us to consider the possibility of the direct-attack mechanism in hdroborations with $BHBr_2{\cdot}SMe_2$. If important with this reagent, it may be important with many other reagents as well. Consequently, we investigated the mechanism of the hydroboration of alkenes and alkynes with $BHBr_2{\cdot}SMe_2$. We report our results in this paper.[1]

Results and Discussion

$BHBr_2{\cdot}SMe_2$ can be obtained in pure form by the reaction of boron tribromide–methyl sulfide with borane–methyl sulfide (eq 1).[3,12] It shows a characteristic B–H

$$BH_3{\cdot}SMe_2 + 2BBr_3{\cdot}SMe_2 \rightarrow 3BHBr_2{\cdot}SMe_2 \qquad (1)$$

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(1) For a preliminary communication, see: Brown, H. C.; Chandrasekharan, J. *Organometallics* **1983**, *2*, 1261.

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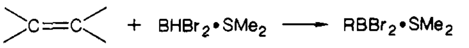
Table I. Rate Data for the Hydroboration of 1-Hexene (0.100 M) with $BHBr_2 \bullet SMe_2$ (0.100 M) in CH_2Cl_2 at 25 °C[a]

time, s	$[BHBr_2{\cdot}SMe_2]$, M	$k_2 \times 10^3$, $M^{-1}\ s^{-1}$
0	0.100	
186	0.089	6.8
306	0.084	6.2
546	0.077	5.5
786	0.072	5.1
1266	0.063	4.6
1986	0.054	4.3
2706	0.047	4.2
4146	0.038	4.0
5586	0.032	3.8
8466	0.024	3.7
10626	0.020	3.7

[a] Doubling the initial concentration of the reactants did not alter the magnitude or the drift appreciably.

stretching absorption at 2500 cm^{-1}. Consequently, we used the quantitative IR procedure[13] to follow all of the hydroboration reactions with $BHBr_2{\cdot}SMe_2$. All of the reactions were done at 25 °C in dichloromethane.

Hydroboration of Alkenes with Dibromoborane–Methyl Sulfide. (a) Mechanistic Considerations. The reaction of alkenes with $BHBr_2{\cdot}SMe_2$ may either proceed by a direct reaction of the alkene with the complex (eq 2)



(2)

or by a prior dissociation of the complex into $BHBr_2$ and Me_2S, followed by the reaction of the free $BHBr_2$ with the alkene to give $RBBr_2$, which will then form a complex with Me_2S formed in the dissociation step (eq 3–5). The direct-attack mechanism is kinetically simple and will lead to second-order kinetics, first order in the alkene and first order in the reagent, while the dissociation mechanism predicts complex kinetics. The rate equation for the dissociation mechanism can be derived by using the steady-state hypothesis (eq 6).[14]

$$BHBr_2{\cdot}SMe_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BHBr_2 + SMe_2 \quad (3)$$

$$BHBr_2 + \text{alkene} \xrightarrow{k_2} RBBr_2 \quad (4)$$

$$RBBr_2 + Me_2S \overset{K'}{\rightleftharpoons} RBBr_2{\cdot}SMe_2 \quad (5)$$

$$\frac{d[RBBr_2{\cdot}SMe_2]}{dt} = \frac{k_1k_2[BHBr_2{\cdot}SMe_2][\text{alkene}]}{k_{-1}(K')^{1/2}[RBBr_2{\cdot}SMe_2]^{1/2} + k_2[\text{alkene}]} \quad (6)$$

(b) Rate Studies. Our kinetic study of the hydroboration of 1-hexene (0.100 M) with $BHBr_2{\cdot}SMe_2$ (0.100 M) in CH_2Cl_2 at 25 °C revealed a typical downward drifting of the second-order rate constants with progress of the reaction (Table I). One possible explanation for this behavior was inhibition of the reaction by the product, $RBBr_2{\cdot}SMe_2$. Accordingly, we studied the effect of adding 1 molar equiv of the product n-hexyl$BBr_2{\cdot}SMe_2$ on the rate of hydroboration of 1-hexene. We observed a significant rate retardation (Figure 1). This rate retardation can be readily accounted for by the dissociation mechanism (eq 3–5). Since $RBBr_2{\cdot}SMe_2$ is a weaker complex than $BHBr_2{\cdot}SMe_2$, it can act as a source of small concentrations of Me_2S which will compete with the alkene for the intermediate, $BHBr_2$. If this is so, addition of Me_2S should decrease the rate of hydroboration even more severely than n-hexyl$BBr_2{\cdot}SMe_2$. Indeed, addition of 1 molar equiv of Me_2S represses the rate of hydroboration by $BHBr_2{\cdot}SMe_2$ very severely (Figure 1). If the reaction proceeds by the direct-attack mechanism (eq 2), the rate of the reaction should be unaffected by the addition of Me_2S or the product.

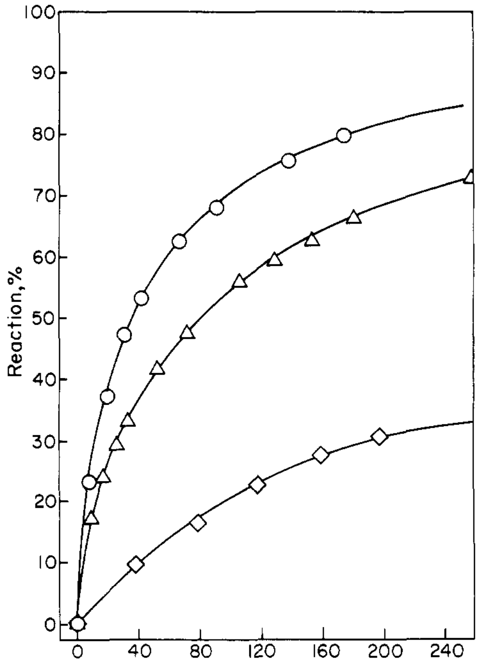


Figure 1. Rate data for the hydroboration of 1-hexene (0.1 M) with $BHBr_2{\cdot}SMe_2$ (0.1 M) in CH_2Cl_2 at 25 °C and the effects of $n\text{-}C_6H_{13}BBr_2{\cdot}SMe_2$ and Me_2S (○, without the addition of Me_2S or $n\text{-}C_6H_{13}BBr_2{\cdot}SMe_2$, $t_{1/2}$ = 39 min; △, in the presence of $n\text{-}C_6H_{13}BBr_2{\cdot}SMe_2$ (0.1 M), $t_{1/2}$ = 78 min; ◇, in the presence of Me_2S (0.1 M), $t_{1/2}$ = 490 min).

Table II. Pseudo-Second-Order Rate Constants for the Hydroboration of 1-Hexene (0.100 M) with $BHBr_2 \bullet SMe_2$ (0.100 M) in the Presence of Me_2S (0.100 M) in CH_2Cl_2 at 25 °C

time, s	$[Br_2BH{\cdot}SMe_2]$, M	$k_2' \times 10^4$, $M^{-1}\ s^{-1}$
0	0.100	
9180	0.083	2.17
13020	0.077	2.29
15960	0.073	2.29
20220	0.069	2.19
24540	0.065	2.16
42300	0.053	2.06
89640	0.034	2.16
	$k_{\text{graphical}}$	2.14

Kinetics of Hydroboration of Alkenes and Alkynes with Dibromoborane–Methyl Sulfide in the Presence of Excess Methyl Sulfide. Our explanation for the inhibiting effect of the product on the hydroboration of alkenes with $BHBr_2{\cdot}SMe_2$ is that the small concentration of Me_2S produced by the incipient dissociation of $RBBr_2{\cdot}SMe_2$ represses the dissociation of $BHBr_2{\cdot}SMe_2$. Since the amount of the product increases with progress of the reaction, the inhibition increases, leading to a downward drifting of the rate constant. If this were so,

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(14) The steady state condition was imposed on $BHBr_2$ and the rate equation was derived for the first two steps (eq 3 and 4) as

$$\text{rate} = \frac{k_1k_2[BHBr_2{\cdot}SMe_2][\text{alkene}]}{k_{-1}[Me_2S] + k_2[\text{alkene}]}$$

$[Me_2S]$ was then replaced by $(K')^{1/2}[RBBr_2{\cdot}SMe_2]^{1/2}$, assuming that eq 5 represents a rapid equilibrium.

Table III. Effect of Concentration of Methyl Sulfide on the Pseudo-Second-Order Rate Constants for 1-Hexene and 2-Methyl-1-pentene in CH_2Cl_2 at 25 °C

initial concn, M			$k_2' \times 10^4$, M^{-1} s^{-1}		
alkene	$BHBr_2 \cdot SMe_2$	Me_2S	2-methyl-1-pentene (1)	1-hexene (2)	$k_2'(1)/k_2'(2)$
0.100	0.100	0.100	65.0	2.14	30
0.100	0.100	0.200	33.0	1.03	32
0.100	0.100	0.300	20.1	0.66	30
0.100	0.100	0.400	15.8	0.54	29
0.200	0.200	0.200		1.09	

clean second-order kinetics should be observed in the presence of a sufficient excess of Me_2S since the moderate inhibition by the product will be replaced by the constant retardation by the Me_2S present. In fact, the reaction of 1-hexene (0.100 M) with $BHBr_2 \cdot SMe_2$ (0.100 M) in the presence of Me_2S displays clean second-order kinetics (Table II). The rate equation for this condition can be derived by using the steady-state hypothesis, as eq 7.[15]

$$-\frac{d[BHBr_2 \cdot SMe_2]}{dt} = \frac{k_1 k_2[\text{alkene}][BHBr_2 \cdot SMe_2]}{k_{-1}[Me_2S]} \quad (7)$$

Since $[Me_2S]$ is practically constant throughout the reaction, the pseudo-second-order rate constant k_2' may be obtained as

$$k_2' = \frac{k_1 k_2}{k_{-1}[Me_2S]} \quad (8)$$

A study of the effect of concentration of Me_2S of k_2' clearly reveals a strict linear dependence between them, as expected from eq 8 (Table III).

The ratio of k_2' of a given pair of alkenes, say 2-methyl-1-pentene and 1-hexene, is essentially independent of the concentration of Me_2S, indicating that the selectivity of $BHBr_2 \cdot SMe_2$ is unaffected by added Me_2S. The fact that the rate, but not the selectivity, of hydroboration is affected by Me_2S is in strict conformity with the dissociation mechanism.

We also studied the kinetics of hydroboration of a number of alkenes and alkynes with $BHBr_2 \cdot SMe_2$ in the presence of excess Me_2S. In all cases studied, good second-order rate behavior was observed (Table IV). In many cases, the ratios of the rate constants are in agreement with the ratios of relative reactivities established earlier by the competitive method (Table IV).[12] In the case of highly reactive alkynes, such as 3-hexyne, a good agreement between the kinetic and relative reactivity data is not realized. In such cases we believe that the kinetic data are far more accurate and represent the true picture.[16] The psuedo-second-order rate constants of the various alkenes and alkynes will help us in a precise understanding of the effect of structure of alkene or alkyne on its reactivity toward $BHBr_2 \cdot SMe_2$.[17]

Catalysis of the Hydroboration of Alkenes with $BHBr_2 \cdot SMe_2$ by Small Quantities of Boron Tribromide. It occurred to us that if the dissociation mechanism is correct, small quantities of an added Lewis acid, say BBr_3, should be able to catalyze the reaction by trapping the free Me_2S. In fact, 5 mol % of BBr_3 catalyzes the hydroboration of 1-hexene with $BHBr_2 \cdot SMe_2$ remarkably (Table V). The catalysis of the hydroboration of alkenes by small quantities of BBr_3 is of immediate use in organic synthesis. Even though $BHBr_2 \cdot SMe_2$ is capable of hydroborating many alkenes at satisfactory rates even in the absence of added Lewis acid, with less reactive alkenes such as cyclohexene, the reaction is very slow, and it is practically impossible to complete the reaction.[18] By using 10 mol % of BBr_3 as the catalyst, we are able to effect the hydroboration of cyclohexene to completion in 6 h in CH_2Cl_2 at reflux temperature (Table V).

Table IV. Kinetic Data for the Hydroboration of Representative Alkenes and Alkynes with $BHBr_2 \cdot SMe_2$ in the Presence of Me_2S in CH_2Cl_2 at 25 °C

compound	$k_2' \times 10^4$, M^{-1} s^{-1} [a]	relative reactivity[b]
3-hexyne	213[c] (104)	4880
4-octyne	158	3560
2-methyl-1-pentene	65.0 (33.0)	2050
cyclooctene	7.65	312
1-hexyne	4.92	234
2-methyl-2-butene	5.48	214
1-methylcyclopentene	2.98	126
1-hexene	2.14 (1.03)	100
1-octene	2.08	95.2
cycloheptene	1.14	66
cis-3-hexene	1.00	42.1
cis-4-methyl-2-pentene	0.565	40.2
3,3-dimethyl-1-butene	0.559	20.1
cyclopentene	0.465	16.5
trans-3-hexene	0.401	22.6
trans-4-methyl-2-pentene	0.197	12.0

[a] For all runs, $[Br_2BH \cdot SMe_2]_{init} = [\text{alkene}]_{init} = 0.100$ M; $[Me_2S]$ was kept at 0.100 M. For the values in parentheses, $[Me_2S] = 0.200$ M. [b] From ref 12. [c] Shows intermediate kinetic behavior.

Table V. Hydroboration of Alkenes with $BHBr_2 \cdot SMe_2$ in the Presence of Catalytic Amounts of BBr_3 in CH_2Cl_2

alkene	BBr_3, mol %	temp, °C	time for completion
1-hexene[b]		25	8 h
1-hexene[c]	5	25	15 min
1-hexene[c]	10	25	5 min
cyclohexene[d]		40	several days
cyclohexene[c]	10	40	6 h

[a] 1.0 M in the reactants. [b] Data for 1-octene taken from ref 10. [c] To the rest of the materials, BBr_3 in CH_2Cl_2, was added dropwise at 0 °C, and the reaction mixture was then raised to the mentioned temperature. [d] The reaction becomes very slow at later stages.

Conclusions

All of our results presented in this paper, namely, the rate retardation by the product and by Me_2S, the second-order kinetics realized in the presence of excess Me_2S and BBr_3 catalysis, consistently point to the dissociation mechanism (eq 3–5) as the correct one for the hydroboration of alkenes with $BHBr_2 \cdot SMe_2$. This mechanism can nicely explain as to why $BHBr_2 \cdot SMe_2$ is able to hydroborate alkenes much faster than does $BHCl_2 \cdot SMe_2$. $RBCl_2 \cdot SMe_2$ is a weaker complex than $RBBr_2 \cdot SMe_2$ since $RBCl_2$ is a weaker Lewis acid than $RBBr_2$. As a result, $RBCl_2 \cdot SMe_2$ dissociates into $RBCl_2$ and Me_2S to a greater extent than does $RBBr_2 \cdot SMe_2$ and thus has a larger rate-retarding effect on the reaction with the alkene. Consequently, we are left with only one problem, viz, the regiochemistry of hydroboration of 2-methyl-2-butene. In

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(15) In the presence of excess Me_2S, $k_{-1}[Me_2S] \gg k_2[\text{alkene}]$. Hence the equation given in ref 14 reduces to eq 7.

(16) The competitive method can become less accurate when the competing alkenes react at very different rates, as for example, 3-hexyne and 1-octene.

(17) For a detailed discussion of the effect of structure on the reactivity of alkenes and alkynes, see ref 12.

(18) We circumvented this problem earlier by doing the hydroboration of cyclohexene with $BHBr_2 \cdot SMe_2$ in the presence of 1 molar equiv of BBr_3. Recently, cyclohexyl BBr_2 has been made conveniently by a redistribution of tricyclohexylborane with BBr_3 in the presence of BMS as the catalyst: Brown, H. C.; Basavaiah, D.; Bhat, N. G. *Organometallics* **1983**, *2*, 1309.

an unrelated development, we had an occasion to reinvestigate the experimental conditions for the hydroboration–oxidation of 2-methyl-2-butene with $BHBr_2 \cdot SMe_2$ and correct the regiochemistry to 99.3:0.7 at the secondary and tertiary carbons, respectively.[19] The corrected regiochemistry does not call for an alternate mechanism at all. Our independent studies on the various dialkylborane dimers[20] and $BH_3 \cdot$Lewis base complexes[7] have shown that they dissociate prior to hydroboration as well. Thus, we are now convinced that the dissociation mechanism is generally applicable to all of the hydroborating agents.

Experimental Section

General procedures for the manipulation of boron reagents have been described.[21] All glassware, syringes, and needles were oven-dried at 140 °C for several hours. The glassware was assembled hot and cooled under a stream of dry nitrogen. Syringes were assembled and fitted with needles while hot and cooled as assembled units.

Materials. $BHBr_2 \cdot SMe_2$ was prepared from $BH_3 \cdot SMe_2$ and $BBr_3 \cdot SMe_2$ by using a reported precedure[3] and was subsequently recrystallized[12] from CH_2Cl_2 at -78 °C. The alkenes were purified by distillation over LAH in a nitrogen atmosphere. The alkynes were purified by distillation in a nitrogen atmosphere. Me_2S was purified by distillation over 9-borabicyclo[3.3.1]nonane in nitrogen atmosphere. CH_2Cl_2 (Baker, analytical reagent grade) was stored over molecular sieves under nitrogen and used as such.

General Procedure for Kinetics Studies. The kinetics were studied by following the concentration of $BHBr_2 \cdot SMe_2$ by measuring the absorbance of the B–H stretching vibration at 2500 cm^{-1} with Miran 1A variable filter infrared spectrometer from Wilks Scientific Corporation. A typical procedure is as follows. To a solution of Me_2S (4.85 mL of 0.515 M) in a 50-mL round-bottom flask were added $BHBr_2 \cdot SMe_2$ in CH_2Cl_2 (1.56 mL, 1.60 M) and CH_2Cl_2 (18.28 mL). After equilibrating at 25.00 ± 0.05 °C (0.5 h), the solution was pumped through a 1-mm NaCl cell at a rate of 4 mL/min to measure the initial absorbance. The reaction was started by adding 1-hexene (0.313 mL) with the help of a syringe. The reactants and Me_2S were 0.100 M each. The absorbance was noted at desired time intervals. When the reactions were sufficiently fast, the absorbance was continuously recorded on a chart paper. On the other hand, when they were slow, the absorbances were noted at some specific time intervals alone. The background absorbance was measured by pumping pure CH_2Cl_2 through the cell. The absorbances were translated into concentrations, and the rate constants were obtained by procedures already published.[13] The rate studies (Figure 1) were also made by the quantitative IR procedure.

Hydroboration of Alkenes with $BHBr_2 \cdot SMe_2$ in the Presence of Catalytic Amounts of Boron Tribromide. The following procedure is representative. To 2.60 mL of $Br_2BH \cdot SMe_2$ in CH_2Cl_2 (1.84 M), *n*-octane (0.3 mL) (internal standard), and CH_2Cl_2 (0.3 mL) was added cyclohexene (0.55 mL, 10% excess). Then BBr_3 (1.0 mL of a 0.5 M solution of CH_2Cl_2) was added dropwise while the reaction mixture was cooled with ice. After being stirred for about 10 min, the reaction mixture was then refluxed. After 6 h, the ^{11}B NMR showed that the reaction is complete. Oxidation with alkaline H_2O_2 and analysis by GC indicated that cyclohexanol was formed in 97% yield.

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Association of α-Alkyl-β,β-dimesitylethenols with Hydrogen Bond Accepting Solvents[1]

Zvi Rappoport,* David A. Nugiel, and Silvio E. Biali

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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The δ(OH) values for α-alkyl-β,β-dimesitylethenols ($Mes_2C{=}C(OH)R$, **2**, R = Me, Et, *i*-Pr, *t*-Bu) were measured in eight solvents and in several binary CCl_4–DMSO-d_6 mixtures. Large shifts to a lower field were observed on increasing the hydrogen bond accepting ability of the solvent or the mixture. The δ(OH) value for **2** in the various solvents were linear with δ(OH) for $Mes_2C{=}CHOH$ (**1**) and approximately linear (with slopes C) with Kamlet–Taft's hydrogen bond accepting parameter β of the solvent. Long-range couplings ^4J(HCCOH) were observed for **2**, *R* = *i*-Pr in several solvents but not in DMSO. The change in δ(OH) in the CCl_4–DMSO-d_6 mixtures was analyzed in terms of formation of a 1:1 association complex of the enol with DMSO and assuming that a syn-type conformer in CCl_4 and an anti-type conformer in DMSO are present in a rapid equilibrium. The δ(OH) for the anti-type conformer ($\delta_{\text{anti}\cdot\text{DMSO}}$) was calculated, but information on its exact geometry is not available. Complete association with DMSO is not achieved even in the pure solvent. The log K_{assoc} values are linearly correlated with the σ^* values and decrease nonlinearly with the increase in the steric parameter E_s. They are linear with the slopes *C* and with $\delta_{\text{anti}\cdot\text{DMSO}}$. The polar effect on K_{assoc} is in the expected direction. The small sensitivity to steric effects is in contrast with the large sensitivity to steric effects found for other mechanistic phenomena on increasing the bulk of R in **1** and **2**. This is presumably due to the occurrence of the association with the hydrogen bond accepting solvent on the relatively unhindered side of the crowded enol molecules.

The conformation of the C=COH moiety and the interaction of the OH group of stable simple enols with hydrogen bond accepting solvents was previously investigated by IR and NMR techniques for several β,β-dimesityl-α-aryl- (and α-H) ethenols.[2] The most extensively studied compound was 2,2-dimesitylethenol (**1**) for which it was concluded from the changes of the coupling constant ^3J(HCOH) and the chemical shift of the enolic proton δ(OH) with the solvent that the conformation of the C=COH moiety around the C–O bond is syn planar (**1a**)

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[1] Part 20 is in the series "Stable Simple Enols". For part 19, see Biali, S. E.; Nugiel, D. A.; Rappoport, Z., submitted to *J. Am. Chem. Soc.* for publication.

[2] Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641.

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