Thermodynamics of Vinyl Ethers. 31. Isomer Equilibria in Some Six- and Seven-Membered Cyclic Dienes[1]

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The relative thermodynamic stabilities of 1,3-cyclohexadiene and 1,4-cyclohexadiene, together with a number of their alkoxy and other derivatives and some related seven-membered cyclic dienes, have been determined by chemical equilibration in Me_2SO and cyclohexane solution at various temperatures. The values of the thermodynamic parameters $\Delta G^\ominus$, $\Delta H^\ominus$, and $\Delta S^\ominus$ for the isomerization processes involved are discussed and show clearly that the apparently conjugated diene system of 1,3-cyclohexadiene is devoid of conjugation, contrary to that of 1,3-cycloheptadiene.

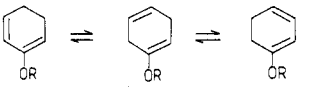
Since the pioneering work of Kistiakowsky et al. on the enthalpies of hydrogenation of miscellaneous olefins it has been known that 1,3-cyclohexadiene (**1a**) does not possess

1a **1b**

the high stability characteristic of many 1,3-dienes such as 1,3-butadiene.[2] The enthalpy of hydrogenation of the gaseous **1a** is only some 7.5 kJ mol^{-1} smaller (less negative) than twice the enthalpy of hydrogenation of gaseous cyclohexene[2]; hence it may be concluded that in **1a** the conjugative stabilization is only about half of the corresponding stabilization in 1,3-butadiene (15 kJ mol^{-1}). However, as the enthalpies of hydrogenation of **1a** and **1b** (1,4-cyclohexadiene) are essentially identical, and as it is hard to realize the presence of any stabilizing factor in the latter, Turner et al.[3] have suggested that **1a** is devoid of conjugation. The same view is supported by a study of the acid-catalyzed hydration of 1,3-cycloalkadienes.[4]

The similar enthalpies of hydrogenation of 1 and **1b** are in line with the results of an equilibrium study[5] showing that also the Gibbs energy difference between **1a** and **1b** is small, the experimental $\Delta G^\ominus$ value of 2.4 kJ mol^{-1} for the **1a** $\rightleftharpoons$ **1b** reaction at 95 °C being mostly (by 2.1 kJ mol^{-1}) due to the higher symmetry of **1b** (according to another equilibrium study, however, the corresponding $\Delta G^\ominus$ value is 1.7 kJ mol^{-1} at 110 °C; see ref 40 of ref 3). Contrary to the opinions of Turner et al.[3] and Jensen et al.,[4] the authors of the equilibration study[5] propose that there is an exceptional stabilization energy of ca. 8 kJ mol^{-1} in **1b**, a stabilization absent in other 1,4-dienes.

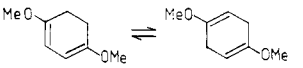
Since the earlier equilibration studies were conducted at a single temperature only, one of the aims of the present study was to determine the values of the equilibrium constant for the **1a** $\rightleftharpoons$ **1b** reaction at several temperatures to be able to calculate the values of $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$ for this isomerization process. Owing to our interest in the thermodynamic stability of alkoxy-substituted olefins (vinyl ethers), we extended the equilibration experiments to include the following monoalkoxy derivatives of **1a** and **1b**:



a **b** **c**

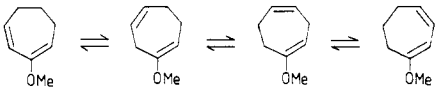
2, R = Me
3, R = *i*-Pr
4, R = Et_2CH

In a previous work of this series,[6] the equilibrium **5a** $\rightleftharpoons$ **5b** was studied. To see the effect of a different ring size



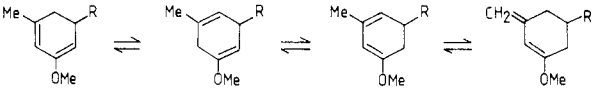
5a **5b**

on the isomer equilibria, reaction **6a** $\rightleftharpoons$ **6b** $\rightleftharpoons$ **6c** $\rightleftharpoons$ **6d** was also included in our study:



6a **6b** **6c** **6d**

In the compounds shown above, the C=C bonds are necessarily endocyclic; in the following reaction, one of the C=C bonds may migrate to an exocyclic position (for **8**,



a **b** **c** **d**

7, R = H
8, R = Me

both of the C=C bonds may be exocyclic but the relative stability of this form, not a vinyl ether, is very poor). This reaction with R = H has been studied earlier in a qualitative sense by Birch et al.[7] who found that sodium amide catalyzes the isomerization of **7b** to **7c** and further to **7d**.

Most of the equilibrations described in this study were carried out in cyclohexane solution with I_2 as catalyst.[8,9] Attempts to employ the same technique to the equilibrium **1a** $\rightleftharpoons$ **1b** resulted in complete disproportionation of the cyclohexadienes to benzene and cyclohexene, a reaction which has previously been found to be catalyzed by tertiary phosphine complexes of zirconium and also by KOBu-*t* in

(1) Part 30: Taskinen, E. *Acta Chem. Scand., Ser. B*, in press.
(2) Kistiakowsky, G. B.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1936**, *58*, 146.
(3) Turner, R. B.; Mallon, B. J.; Tichy, M.; Doering, W. von E.; Roth, W. R.; Schröder, G. *J. Am. Chem. Soc.* **1973**, *95*, 8605.
(4) Jensen, J. L.; Uaprasert, V. *J. Org. Chem.* **1976**, *41*, 649.
(5) Bates, R. B.; Carnighan, R. H.; Staples, C. E. *J. Am. Chem. Soc.* **1963**, *85*, 3030.
(6) Taskinen, E. *Acta Chem. Scad., Ser. B* **1974**, *28*, 201.
(7) Birch, A. J.; Shoukry, E. M. A.; Stansfield, F. *J. Chem. Soc.* **1961**, 5376.
(8) Rhoads, S. J.; Chattopadhyay, J. K.; Waali, E. E. *J. Org. Chem.* **1970**, *35*, 3352.
(9) Taskinen, E. *J. Chem. Thermodyn.* **1973**, *5*, 783.

0022-3263/85/1950-4844$01.50/0

Table I. Thermodynamic Data at 298.15 K for the Reactions Studied in This Work

reaction	$\Delta G^\ominus$/kJ mol^{-1}	$\Delta H^\ominus$/kJ mol^{-1}	$\Delta S^\ominus$/J K^{-1} mol^{-1}
1a → 1b	1.48 ± 0.16	−1.6 ± 0.8	−10.2 ± 2.2
2a → 2b	−5.0 ± 0.4	−7.0 ± 1.5	−7.0 ± 4
3a → 3b	−4.37 ± 0.28	−6.9 ± 1.4	−9.0 ± 4
4a → 4b	−4.49 ± 0.20	−8.2 ± 1.0	−12.5 ± 2.7
5a → 5b[b]	2.06 ± 0.01	0.2 ± 0.2	−6.4 ± 0.6
7a → 7b	−0.2 ± 0.8	−1.0 ± 3	−3.0 ± 8
8a → 8b	−0.08 ± 0.16	−1.3 ± 0.8	−4.0 ± 2.2
2b → c	−3.80 ± 0.11	−2.1 ± 0.5	5.5 ± 1.3
3b → 3c	−4.55 ± 0.09	−3.2 ± 0.4	4.5 ± 1.2
4b → 4c	−4.1 ± 0.3	−0.7 ± 1.5	11.0 ± 4
7b → 7c	−4.0 ± 0.4	−3.9 ± 1.4	0 ± 4
8b → 8c	−4.41 ± 0.15	−4.4 ± 0.7	0 ± 2.0
2a → 2c	−8.78 ± 0.22	−9.1 ± 0.8	−1.0 ± 2.0
3a → 3c	−8.80 ± 0.12	−9.6 ± 0.6	−2.8 ± 1.6
4a → 4c	−8.61 ± 0.14	−8.9 ± 0.7	−1.0 ± 1.9
7a → 7c	−4.3 ± 0.5	−4.9 ± 1.9	−2.0 ± 5
8a → 8c	−4.48 ± 0.03	−5.71 ± 0.14	−4.1 ± 0.4
6a → 6d	−8.00 ± 0.12	−7.8 ± 0.5	0.8 ± 1.2
7d → 7c	2.3 ± 0.5	5.9 ± 2.2	12.0 ± 6
8d → 8c	1.64 ± 0.04	4.6 ± 0.2	9.9 ± 0.5

[a] Solvents: Me_2SO for 1, cyclohexane for 2–8. The errors are twice the standard errors. [b] Reference 6.

Me_2SO.[10,11] In spite of these discouraging reports, we tested the latter reagent to catalyze the reaction **1a** ⇌ **1b** and found that although prolonged reaction times undoubtedly lead only to the disproportionation products, the thermodynamic equilibrium between **1a** and **1b** is quickly established and consistent values of the equilibrium constant were readily obtained from any initial mixture of the isomeric forms.

Results and Discussion

The results of the equilibration experiments are summarized in Table I, together with literature data for the reaction **5a** → **5b**. The equilibrium concentrations of the 1,4 isomers of **6** (**6b**, **6c**) were so low that the presence of these compounds in the equilibrium mixture could not be detected; hence thermodynamic data are given only for the **6a** → **6d** reaction. For the four isomeric forms of **7** and **8** given above, six different isomerization reactions are possible but in Table I thermodynamic data are given for just four (the most interesting ones) of them.

Our equilibration results for **1a** → **1b** confirm the previous conclusions of the higher thermodynamic stability of the conjugated form **1a** (ref 5 and ref 40 of ref 3). In addition, the values of $\Delta H^\ominus$ and $\Delta S^\ominus$ lead to a $\Delta G^\ominus$ value of 2.2 kJ mol^{-1} for **1a** → **1b** in Me_2SO solution at 95 °C, in nice agreement with the equilibration data of Bates et al.[5] which suggest a $\Delta G^\ominus$ value of 2.1 kJ mol^{-1} in *tert*-amyl alcohol at the same temperature. The higher thermodynamic stability of **1a**, however, is only a consequence of the higher symmetry of **1b**: the symmetry numbers of **1a** and **1b** are 2 and 4, respectively. If the values of $\Delta G^\ominus$ and $\Delta S^\ominus$ are corrected for the different symmetries of the species involved, they must be written as −0.24 kJ mol^{-1} and −4.4 J K^{-1} mol^{-1} (at 298.15 K), respectively, instead of the values 1.48 kJ mol^{-1} and −10.2 J K^{-1} mol^{-1} given in Table I, i.e., the nonconjugated isomer has the lower Gibbs energy value. This agrees with the relative thermochemical stabilities, the value of $\Delta H^\ominus$ for the **1a** → **1b** reaction being −1.6 ± 0.8 kJ mol^{-1}. For comparison, the enthalpies of hydrogenation of **1a** and **1b** (to cyclohexane) are −224.4 ± 1.2 and −225.5 ± 1.4 kJ mol^{-1}, respectively, in acetic acid at 25 °C.[3] In view of the magnitudes of the experimental uncertainties involved and the different solvents used, our equilibration data are in complete agreement with these values. The similar enthalpy contents of **1a** and **1b** are surprising, especially if we consider that in the apparently related isomer pair 1,2-dihydronaphthalene–1,4-dihydronaphthalene the enthalpy of the conjugated isomer is about 13 kJ mol^{-1} lower than that of the nonconjugated form.[12]

On going to the monoalkoxy derivatives **2** to **4**, the higher symmetry of the 1,4 form is destroyed and two isomeric 1,3 forms arise. In a thermodynamic as well as thermochemical sense, the conjugated **c** form is seen to be the most stable and the conjugated **a** form the least stable species. The marked difference in stability between the 1,3 isomers is noteworthy: for each **a** → **c** reaction studied, the value of $\Delta H^\ominus$ is consistently ca. −9 kJ mol^{-1} (and the corresponding entropy change slightly negative, −1.6 J K^{-1} mol^{-1} on average). Qualitatively, the higher stability of the **c** isomer is understandable since in this form the olefinic linkage between C-3 and C-4 is capable of extending the conjugation in the vinyloxy group:

$$\text{-O-C=C-C=C} \leftrightarrow \text{-}\overset{+}{\text{O}}\text{=C-C=C-}\overset{-}{\text{C}}$$

This effect is not possible in the **a** isomer. In fact, it appears that conjugation in the vinyloxy group of the **a** form is actually disturbed (weakened) by the presence of the second C=C bond since the reactions **2a** → **2b**, **3a** → **3b**, and **4a** → **4b** are clearly more exothermic than the reaction **1a** → **1b**.

For the 1,4 → 1,3 isomerization reactions **1b** → **1a**, **2b** → **2c**, and **5b** → **5a**, the values of $\Delta H^\ominus$ are 1.6, −2.1, and −0.2 kJ mol^{-1}, respectively. Accordingly, although a single MeO substituent at the terminal carbon atom of a C=C—C=C system increases the relatively stability of the 1,3 isomer by ca. 4 kJ mol^{-1}, the presence of two MeO substituents at the opposite terminal carbons has a stabilizing effect of only 2 kJ mol^{-1} on the 1,3 form. This is understandable since the conjugative effects of the two MeO groups are affecting into opposite directions whereby their stabilizing effects on the 1,3 form are largely cancelled.

As mentioned above, the thermodynamic stability of the 1,4 isomers of the seven-membered carbocyclic dienes (**6b**,**6c**) was too low to allow the detection of their presence in the equilibrium mixtures. This is reasonable since according to the thermochemical data of Turner et al.,[3] the value of $\Delta H^\ominus$ for the 1,4 → 1,3 isomerization of the parent hydrocarbon cycloheptadiene is ca. −25 kJ mol^{-1} at 25 °C. On the other hand, for **6a** → **6d** the values of the thermodynamic parameters of isomerization do not essentially deviate from those for the related reaction between the six-membered dienes.

Astonishing changes in the thermodynamic data for the **a** → **b** reaction are observed on going from the compounds **4**–**6** to **7** and **8**: the reaction becomes ca. 6 kJ mol^{-1} less exothermic and the reaction entropies appear to increase by ca. 6 J K^{-1} mol^{-1}. In fact, the thermodynamic data for the **7a** → **7b** and **8a** → **8b** reactions are comparable with those for **1a** → **1b**, provided that the $\Delta G^\ominus$ and $\Delta S^\ominus$ values of the latter reaction are corrected for the higher symmetry of **1b**. The increased relatively stability of the **a** isomer due to methyl substitution at the olefinic linkage is also reflected (although to a lesser extent) in the thermodynamic data for the **7a** → **7c** and **8a** → **8c** reactions: the

(10) Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941.
(11) Hofmann, J. E.; Argabright, P. A.; Schriesheim, A. *Tetrahedron Lett.* **1964**, 1005.
(12) Williams, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 1395.

exothermicity is decreased by 3 to 4 kJ mol^{-1}. These trends are difficult to explain.

Finally, let us consider the thermodynamics of the double bond exo → endo isomerization represented by the **d** → **c** reaction (**7**, **8**). The endo forms **7c** and **8c** are seen to be favored by higher entropy values ($\Delta S^{\ominus} \sim 10$ J K^{-1} mol^{-1}) but disfavored by higher enthalpy values ($\Delta H^{\ominus} =$ 5 kJ mol^{-1}). It is interesting to compare the thermodynamics of this reaction with that for the exo → endo isomerization of methylenecyclohexane. In acetic acid at 298.15 K, the reaction enthalpy is ca. −10.0 kJ mol^{-1} and the Gibbs energy change $\Delta G^{\ominus}$ ca. −13.6 kJ mol^{-1} for the latter reaction.[13,14] From these values the reaction entropy is obtained to be about 12 J K^{-1} mol^{-1}. Another related isomerization reaction is provided by the reaction 4-methylene-1,3-dioxane → 4-methyl-1,3-diox-4-ene for which $\Delta S^{\ominus} = 12.8 \pm 2.3$ J K^{-1} mol^{-1} (cyclohexane solution, 298.15 K).[15] The values of $\Delta S^{\ominus}$ quoted are all similar although a higher entropy change might have been expected for the isomerization of methylenecyclohexane to 1-methylcyclohexene because of the higher symmetry of the reactant in this case (external symmetry number = 2). A comparison of the reaction enthalpies of the carbocyclic compounds is, however, more rewarding. The values of $\Delta H^{\ominus}$ for the **d** → **c** reaction are ca. 15 kJ mol^{-1} more positive than that for methylenecyclohexane → 1-methylcyclohexene. The big difference in reaction enthalpies for the formally similar reactions shows clearly that the high conjugative stabilization likely to exist in the exo forms **7d** and **8d** (cf. ref 16 for related acyclic compounds) is (almost) completely lost on going to the 1,3-cyclohexadiene system of the endo isomers (for comparison, the conjugative stabilization in 1,3-butadiene is ca. 15 kJ mol^{-1}, ref 2). Hence our equilibration experiments confirm the conclusions of Turner et al.[3], viz. the 1,3-cyclohexadiene system is devoid of conjugation.

Experimental Section

Materials. 1,3-Cyclohexadiene (**1a**) and 1,4-cyclohexadiene (**1b**) are commercially available (Aldrich).

2-Methoxy-1,3-cyclohexadiene (2a), 1-Methoxy-1,4-cyclohexadiene (2b), and 1-Methoxy-1,3-cyclohexadiene (2c). The dimethyl acetal of 2-cyclohexen-1-one was prepared from the ketone and trimethyl orthoformate in MeOH by the method of House and Kramar.[17] The reaction mixture was kept overnight at room temperature after which it was made alkaline (NaOMe), followed by distillation at reduced pressure (ca. 15 torr). During distillation the acetal decomposed into MeOH and a mixture of the 1,3 isomers **2a** and **2c** (in the mole ratio 1:3), bp 32–36 °C (15 torr). The yield was 52%. If the crude reaction mixture was not made alkaline prior to distillation, a 1:2 mixture of **2c** and **2b** was obtained in 40% yield, bp 70–72 °C (55 torr).

2-Isopropoxy-1,3-cyclohexadiene (3a), 1-Isopropoxy-1,4-cyclohexadiene (3b), and 1-Isopropoxy-1,3-cyclohexadiene (3c). These compounds were obtained in low yield from **2c** by an alcohol exchange reaction with *i*-PrOH, bp 55–61 °C (12–20 torr).

2-(3-Pentoxy)-1,3-cyclohexadiene (4a), 1-(3-Pentoxy)-1,4-cyclohexadiene (4b), and 1-(3-Pentoxy)-1,3-cyclohexadiene. See the preparation of **3a–3c**. The reaction mixture was diluted with an approximately equal volume of quinoline to avoid polymerization. Bp 83–85 °C (10 torr).

2-Methoxy-1,3-cycloheptadiene (6a), 2-Methoxy-1,4-cycloheptadiene (6b), 1-Methoxy-1,4-cycloheptadiene (6c), and 1-Methoxy-1,3-cycloheptadiene (6d). See the preparation of **2a–2c**. The yield was 65%, bp 60–65 °C (19 torr).

3-Methoxy-1-methyl-1,3-cyclohexadiene (7a), 4-Methoxy-2-methyl-1,4-cyclohexadiene (7b), 1-Methoxy-3-methyl-1,3-cyclohexadiene (7c), and 1-Methoxy-3-methylenecyclohexene (7d). See the preparation of **2**. The reaction mixture was diluted with twice its volume of hexane to minimize polymerization. After the acetal formation was complete, the reaction mixture was made alkaline with NaOMe and distilled at ca. 10 torr. The acetal decomposed into MeOH and a mixture of **7a–7d**, bp 57–66 °C (14 torr).

3-Methoxy-1,5-dimethyl-1,3-cyclohexadiene (8a), 4-Methoxy-2,6-dimethyl-1,4-cyclohexadiene (8b), 1-Methoxy-3,5-dimethyl-1,3-cyclohexadiene (8c), and 1-Methoxy-5-methyl-3-methylenecyclohexene (8d). See the preparation of **7**. The yield of a mixture of **8a–8d**, bp 59–69 °C (11 torr), was ca. 20%.

The crude distillation products were further fractionated using a Perkin-Elmer M 251 Auto Annular Still to gain pure compounds or mixtures of isomers with sufficiently different compositions for spectral characterization and the equilibrations.

Compound Characterization. In general, the structures of the compounds studied were assigned from their ^{1}H NMR and ^{13}C NMR spectra. The spectra of **3a** and **8a**, however, could not be obtained due to the low concentrations of these compounds in the synthetic products. Hence they were identified solely by their retention times in the gas chromatographic analysis of the equilibrium mixtures: the chromatograms of, for example, a mixture of **3a–3c** were remarkably similar to those of the related mixtures of **2a–2c** and **4a–4c**. Since most of the spectra were recorded on mixtures of isomers rather than on pure compounds, all of the NMR signals of the minor component(s) could not always be assigned with certainty. As the carbon spectra are more informative for and characteristic of the compounds studied than the proton spectra, only the former are given in the following.

^{13}C NMR Spectra (15 MHz, $CDCl_3$, δ Values in ppm from Internal Me_4Si). **1a**: 124.4 (C-1,C-4), 126.3 (C-2,C-3), 22.1 (C-5,C-6). **1b**: 124.4 (C-1,C-2,C-4,C-5), 25.9 (C-3,C-6). **2a**: 91.4 (C-1), 153.5 (C-2), 129.2 (C-3), 124.4 (C-4), 21.4 (C-5), 23.1 (C-6), 53.9 (MeO). **2b**: 152.9 (C-1), 90.7 (C-2), 26.4 (C-3), 123.3 (C-4), 124.6 (C-5), 28.5 (C-6), 53.7 (MeO). **2c**: 158.9 (C-1), 92.5 (C-2), 124.4 (C-3), 117.9 (C-4), 23.7 (C-5), 26.9 (C-6), 54.4 (MeO). **3b**: 150.2 (C-1), 92.3 (C-2), 26.4 (C-3), 123.5 (C-4), 124.6 (C-5), 29.1 (C-6), 67.2 (-OCH<), 21.8 (Me). **3c**: 156.4 (C-1), 93.5 (C-2), 124.6 (C-3), 117.1 (C-4), 23.7 (C-5), 27.6 (C-6), 68.3 (-OCH<), 21.8 (Me). **4a**: 92.9 (C-1), 151.6 (C-2), 129.0 (C-3), 124.7 (C-4), 21.6 (C-5), 23.1 (C-6), 78.0 (-OCH<), 25.9 (CH_2), 9.6 (Me). **4b**: 150.9 (C-1), 92.2 (C-2), 26.6 (C-3), 123.6 (C-4), 124.6 (C-5), 29.0 (C-6), 77.5 (-OCH<), 26.0 (CH_2), 9.7 (Me). **4c**: 157.2 (C-1), 93.4 (C-2), 124.7 (C-3), 117.1 (C-4), 23.8 (C-5), 27.5 (C-6), 78.4 (-OCH<), 25.9 (CH_2), 9.6 (Me). **6a**: 162.7 (C-1), 94.7 (C-2), 126.8 (C-3), 122.6 (C-4), 31.0 (C-5), 23.9 (C-6), 34.9 (C-7), 54.5 (MeO). **6d**: 101.0 (C-1), 153.9 (C-2), 133.7 (C-3), 126.2 (C-4), 54.5 (MeO). **7a**: 121.6 (C-2), 88.4 (C-4), 22.0 (C-5), 29.0 (C-6), 53.9 (MeO). **7b**: 118.9 (C-1), 130.5 (C-2), 33.3 (C-3), 153.1 (C-4), 90.4 (C-5), 26.9 (C-6), 22.8 (2-Me), 53.8 (MeO). **7c**: 159.2 (C-1), 96.0 (C-2), 132.0 (C-3), 112.6 (C-4), 23.7 (C-5), 27.0 (C-6), 22.0 (3-Me), 54.4 (MeO). **7d**: 160.1 (C-1), 99.5 (C-2), 143.5 (C-3), 28.3 (C-4), 30.9 (C-6), 105.3 (=CH_2), 54.3 (MeO). **8b**: 126.4 (C-1), 33.3 (C-3), 153.8 (C-4), 97.3 (C-5), 22.6 (Me), 53.8 (MeO). **8c**: 158.6 (C-1), 95.5 (C-2), 131.0 (C-3), 119.7 (C-4), 29.9 (C-5), 35.4 (C-6), 20.3 (Me), 21.9 (Me), 54.3 (MeO). **8d**: 159.6 (C-1), 99.0 (C-2), 144.3 (C-3), 36.4 (C-4), 29.0 (C-5), 39.2 (C-6), 105.5 (=CH_2), 21.1 (5-Me), 54.3 (MeO).

Equilibrations. The reaction **1a** ⇌ **1b** was studied in Me_2SO solution (ca. 20% v/v) with KOBu-*t* (ca. 5 mass %) as catalyst. For other isomer equilibria, cyclohexane was used as the solvent and I_2 as the catalyst.[8,9] The equilibrated samples were analyzed by GLC using Carbowax 20 M packed columns and XE-60 capillary columns. The reaction **1a** ⇌ **1b** was followed at 5 temperatures from 26 to 150 °C, reaction **2a** ⇌ **2b** ⇌ **2c** at 4 temperatures from 100 to 170 °C (the equilibrium **2b** ⇌ **2c**, however, was studied at 2 additional temperatures down to 23 °C), reaction **3a** ⇌ **3b** ⇌ **3c** at 5 temperatures from 26 to 150 °C, reaction **4a** ⇌ **4b** ⇌ **4c** at 5 temperatures from 26 to 150 °C, reaction **6a** ⇌ **6b** ⇌ **6c** ⇌ **6d** at 6 temperatures from 27 to 170 °C, reaction **7a** ⇌ **7b** ⇌ **7c** ⇌ **7d** at 5 temperatures from 60 to 170 °C, and

(13) Turner, R. B.; Garner, R. H. *J. Am. Chem. Soc.* **1958**, *80*, 1424.
(14) Cope, A. C.; Ambros, D.; Ciganek, E.; Howell, C. F.; Jacura, Z. *J. Am. Chem. Soc.* **1960**, *82*, 1750.
(15) Taskinen, E. *Acta Chem. Scand., Ser. B* **1974**, *28*, 1234.
(16) Taskinen, E.; Kuusisto, M. *Acta Chem. Scand., Ser. B* **1980**, *34*, 571.
(17) House, H. O.; Kramar, V. *J. Org. Chem.* **1963**, *28*, 3362.

reaction 8a ⇌ 8b ⇌ 8c ⇌ 8d at 6 temperatures from 26 to 170 °C. In all cases, the position of equilibrium was approached from at least two initial mixtures of isomers with sufficiently different isomer compositions (for 1a ⇌ 1b, for example, pure 1a, pure 1b, and a 1:1 mixture of these forms were used). The values of the thermodynamic parameters were evaluated by linear least-squares treatments of ln K vs. T^{-1}.

Registry No. 1a, 592-57-4; 1b, 628-41-1; 2a, 30979-68-1; 2b, 2886-59-1; 2c, 2161-90-2; 3a, 98677-91-9; 3b, 28495-27-4; 3c, 28495-28-5; 4a, 98677-92-0; 4b, 98677-93-1; 4c, 98677-94-2; 6a, 98677-95-3; 6d, 98677-96-4; 7a, 98677-97-5; 7b, 13697-84-2; 7c, 2161-93-5; 7d, 2773-58-2; 8a, 98677-98-6; 8b, 53922-67-1; 8c, 69697-78-5; 8d, 69697-81-0; *i*-PrOH, 67-63-0; 2-cyclohexen-1-one dimethyl acetal, 1728-18-3; 3-pentanol, 584-02-1.

Onium Ions. 33. (Trimethylsilyl)- and [(Trimethylsilyl)methyl]oxonium and -halonium Ions[1]

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A series of (trimethylsilyl)- and [(trimethylsilyl)methyl]oxonium and -halonium ions were prepared under stable ion conditions by alkylating the corresponding trialkylsilyl ethers or halides. The ions were studied by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The trend of observed ^{13}C NMR shift deshielding effects indicates little charge delocalization occurring due to the α- or β-trialkylsilyl substituents as compared with parent alkyloxonium and -halonium ions. The [(trimethylsilyl)methyl]- and (trimethylsilyl)oxonium salts could be isolated and were found to be stable even at room temperature. These ions act as alkylating agents and were used in related studies as precursors for generation of dialkyloxonium methylides. [(Trimethylsilyl)methyl]halonium ions could be prepared and studied only at low temperature (−78 °C). Raising the temperature and attempting to isolate the halonium ions cause disproportionation. The [(trimethylsilyl)methyl]halonium ions were found to readily alkylate ethers at low temperature, but no trialkylsilylation was observed.

In recent years silylated reagents have gained extensive use in synthetic organic chemistry as well as in mechanistic and structural studies. In the area of silylated reactive intermediates it has been shown that carbocations containing β-(trialkylsilyl)methyl groups exhibit increased stability. This stabilization has been attributed to the strong inductive electron release by the β-trialkylsilyl groups as well as through hyperconjugation between the β Si–C bond and the empty p orbital of the carbocationic carbon.[2,3] Hyperconjugation (σ–π) has been shown in cases where the Si–C bond can achieve a transcoplanar arrangement with the empty 2p orbital of the carbocationic center.[4]

α-Silyl-substituted carbocations have been prepared under stable ion conditions and studied by ^{1}H as well as by ^{13}C and ^{29}Si NMR spectroscopy.[5,6] The ^{13}C NMR chemical shifts of α-silyl-substituted carbocations have been shown to be substantially deshielded as compared to their parent carbon analogues. This deshielding has been attributed to the somewhat bulkier trimethylsilyl group decreasing the necessary overlap for charge delocalization to occur. Previous experimental studies have shown that an α-trialkylsilyl substituent acts as a weak electron acceptor apparently due to hyperconjugation and as an electron donor due to its inductive effect.[7]

In contrast to α- and β-trialkylsilyl-substituted carbocations, silyl-substituted halonium and oxonium ions were yet unknown and present a different situation due to the absence of a vacant p orbital at the cationic center required for pπ–dπ hyperconjugation to occur.

Recently we reported the use of β-trimethylsilyl-substituted oxonium ions in the fluorine induced formation and study of reactive dimethyloxonium methylide.[8] In

$$(CH_3)_3SiCH_2O^+(CH_3)_2 \xrightarrow{F^-} (CH_3)_3SiF + [^-CH_2O^+(CH_3)_2]$$

an analogous manner the preparation of alkylhalonium methylides from β-(trimethylsilyl)halonium ions has been attempted.[9] To date, few details of the preparation and study of silylated oxonium and halonium ions have been reported.

In our continued study of onium ions we now report the preparation under stable ion conditions, reactivity, and NMR spectroscopic (^{1}H, ^{13}C, ^{29}Si) study of a series of α- and β-trialkylsilyl-substituted oxonium and halonium ions.

Results and Discussion

Methyl[(trimethylsilyl)methyl]halonium ions were prepared in a manner analogous to that previously used by

(1) For part 32, see: Olah, G. A.; Herges, R.; Felberg, J. D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1985**, *107*, 5282.
(2) Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc. B* **1969**, 852.
(3) Reynolds, W. F.; Haner, G. K.; Bassindele, A. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 971.
(4) Traylor, T. G.; Honstein, W.; Berwin, H. J.; Clinton, N. J.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5717.
(5) Hairston, T. J.; O'Brien, D. H. *J. Organomet. Chem.* **1971**, *29*, 79. Brook, A. G.; Pannell, K. H. *Can. J. Chem.* **1970**, *48*, 3679.
(6) Olah, G. A.; Berrier, A. L.; Field, L. D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1349.
(7) Adcock, W.; Aldous, G. L. *Tetrahedron Lett.* **1978**, 3387 and references therein. Freeburger, M. E.; Spialter, L. *J. Am. Chem. Soc.* **1971**, *93*, 1894 and references therein. Cutress, N. C.; Katritzky, A. R.; Eaborn, C.; Walton, D. R. M.; Topson, R. D. *J. Organomet. Chem.* **1972**, *43*, 131 and references therein.
(8) Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.* **1984**, *49*, 2112.
(9) Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 4975.

0022-3263/85/1950-4847$01.50/0