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THERMODYNAMICS OF VINYL ETHERS—XXVII†

THERMODYNAMIC STABILITY OF β-METHOXY-SUBSTITUTED α,β-UNSATURATED KETONES AND THE CORRESPONDING CARBOXYLIC ESTERS

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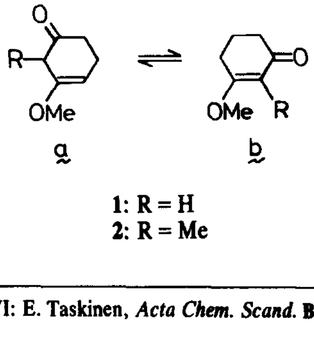
Abstract—Chemical equilibration studies on isomeric β-methoxy-substituted α,β- and β,γ-unsaturated ketones and the corresponding carboxylic esters have been carried out. The α,β-isomers are highly favored at equilibrium if the MeO and keto (or ester) groups are *trans* disposed across the C=C bond and if these groups are unhindered by steric factors to conjugate with the olefinic bond. In acyclic ketones and esters the latter condition is not fulfilled if substituents essentially larger than hydrogen are bound to both C-α and C-β.

In previous papers,[1-6] we have studied the ability of various substituents X (X = alkyl, substituted alkyl, phenyl, halogen, alkoxy, vinyl) to stabilize the olefinic system of α,β-unsaturated (vinyl) ethers.

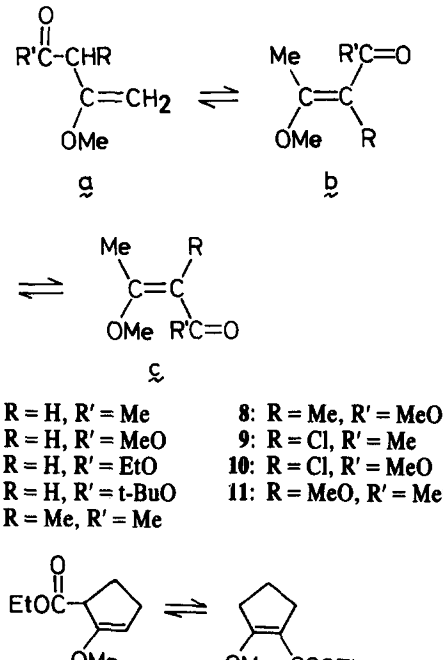
$$-O-C{=}C-X.$$

β-Alkoxy-α,β-unsaturated ketones and the corresponding carboxylic esters may be regarded as substituted vinyl ethers with the moiety C(Y)=O (Y = alkyl, alkoxy) as the substituent X. Very little is known about the thermodynamic stability of these compounds. A decade ago, Rhoads *et al.*[7,8] published a quantitative study of the thermodynamic stability of a few representatives of β-methoxy-α,β-unsaturated esters. Maybe the most significant observation of these equilibration experiments was that a *cis* juxtaposition of MeO and COOMe groups in unsaturated acyclic and 6-membered cyclic compounds gives rise to a surprisingly destabilized system, see $\Delta G^\circ(373\,K) = -15\,kJ\,mol^{-1}$ for the *cis* to *trans* isomerization of the Me ester of 3-methoxypropenoic acid in cyclohexane solution.[7] Similarly, a *cis* juxtaposition of MeO and acetyl groups is also unadvantageous, since $\Delta G^\circ(373\,K) \leqq -14\,kJ\ mol^{-1}$ for the *cis*→*trans* reaction of 4-MeO-3-buten-2-one (neat liquid).[9] Isomer equilibria in the systems **1**-**12** have now been studied to gain more data on the thermodynamic stability of the title compounds.



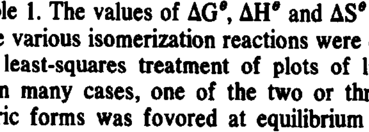
(1)

1: R = H
2: R = Me



(2)

3: R = H, R' = Me
4: R = H, R' = MeO
5: R = H, R' = EtO
6: R = H, R' = t-BuO
7: R = Me, R' = Me
8: R = Me, R' = MeO
9: R = Cl, R' = Me
10: R = Cl, R' = MeO
11: R = MeO, R' = MeO



(3)

12a **12b**

RESULTS AND DISCUSSION

The results of the equilibration experiments are shown in Table 1. The values of ΔG°, ΔH° and ΔS° at 298.15 K for the various isomerization reactions were obtained by linear least-squares treatment of plots of ln K against T^{-1}. In many cases, one of the two or three possible isomeric forms was fovored at equilibrium to such an extent that the presence of the other isomer(s) could not be detected by GLC and ^1H NMR spectrometric analysis of the equilibrium mixture. Hence only the limiting values of K and ΔG° can be given to those reactions. For example, for **1a** ⇌ **1b** $K(b/a) \geqq 100$ and thus $\Delta G^\circ \leqq -14$ kJ mol^{-1} at 373 K.

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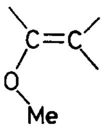
†Part XXVI: E. Taskinen, *Acta Chem. Scand.* **B34**, 643 (1980).

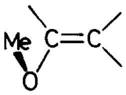
The equilibration data for **1–6** reveal the high thermodynamic stability of the O–C=C–C=O system of the **b** isomers over the non-conjugated double-bond system in the *β,γ*- (**a**) isomers, as well as that of the *trans* configuration of the O–C=C–C=O moiety (in **3–6**) relative to the *cis*. The high thermodynamic stability of the **b** form may probably be ascribed to strong p–π–π conjugation in these compounds:

$$-\ddot{O}-C=C-C=\ddot{O} \leftrightarrow -\overset{+}{O}=C-\overset{-}{\ddot{C}}-C=\ddot{O} \leftrightarrow -\overset{+}{O}=C-C=C-\overset{-}{\ddot{O}}:$$

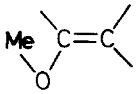
The extent of conjugation is likely to be most pronounced in **1b**, since (a) the MeO group can assume the energetically most favorable planar s-*cis* conformation (the most stable conformation of methyl vinyl ether[10]), (b) the two π-systems are coplanar (the ring carbons, excluding C-5, lie in the same plane, cf. the structure of 2-cyclohexen-1-one[11]), and (c) the MeO and C=O groups are *trans* disposed across the C=C bond. On the other hand, the MeO group of **2b** cannot adopt the s-*cis* structure because of heavy steric crowding with the Me group at C-2. Thus the MeO group is forced to assume either the nonplanar gauche or the planar s-*trans* structure, both of which are energetically less favorable (dipole moment data[12] point to a practically planar s-*trans* conformation). In the ketone **3b**, the acetyl group is known[13,14] to prefer the s-*cis* conformation about the C(sp^2)–C(sp^2) single bond. However, the two double bonds are probably not strictly coplanar since the related compounds, ethylideneacetone **13** and mesityloxide **14**, are calculated to have a twisted conformation with angles of rotation (ω) from the planar s-*cis* structure of 12.9 and 18.8°, respectively.[15] The ester **17** is also reported[16] to have the s-*cis* conformation about the C(sp^2)–C(sp^2) single bond and, by analogy, the same structure might be proposed for **4b**, **5b** and **6b**.



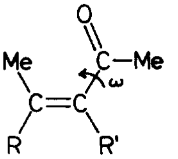
s-*cis*



gauche



s-*trans*



13: R = R′ = H
14: R = Me, R′ = H
15: R = H, R′ = Me
16: R = R′ = Me

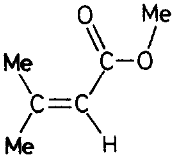


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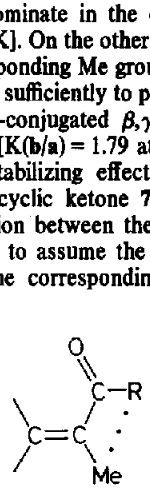
Table 1. Thermodynamic data (T = 298.15 K unless otherwise stated) for the reactions studied in this work. The errors are twice the standard errors

Reaction	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}	Solvent
1a → **1b** to **6a** → **6b**	≤ -14[a]			c-Hx, CCl_4
7a → **7b**	-1.44 ± 0.05	-3.6 ± 0.4	-7.2 ± 1.2	c-Hx
8a → **8b**	-6.88 ± 0.14	-9.1 ± 0.7	-7.3 ± 1.8	c-Hx
9a → **9b**	-7.54 ± 0.18	-10.5 ± 1.0	-10.0 ± 2.7	CCl_4
10a → **10b**	-7.99 ± 0.21	-14.4 ± 1.0	-21.5 ± 2.7	CCl_4
11a → **11b**	-5.59 ± 0.01	-5.3 ± 0.1	1.0 ± 0.1	CCl_4
12a → **12b**	-2.30 ± 0.03	-3.5 ± 0.2	-4.1 ± 0.5	c-Hx
3b → **3c** to **6b** → **6c**	≥14[a]			c-Hx, CCl_4
7b → **7c**	3.62 ± 0.03	-0.5 ± 0.2	-13.6 ± 0.6	c-Hx
8b → **8c**	8.38 ± 0.05	7.2 ± 0.3	-3.9 ± 0.7	c-Hx
9b → **9c**	14[a]			CCl_4
10b → **10c**	8.65 ± 0.26	13.8 ± 1.3	17.2 ± 3.4	CCl_4
11b → **11c**	5.55 ± 0.03	7.2 ± 0.2	5.5 ± 0.4	CCl_4
7a → **7c**	2.12 ± 0.04	-4.0 ± 0.3	-20.9 ± 1.0	c-Hx
8a → **8c**	1.49 ± 0.22	-1.9 ± 1.1	-11.2 ± 2.9	c-Hx
9a → **9c**	≥6.2[a]			CCl_4
10a → **10c**	0.65 ± 0.01	.-0.7 ± 0.1	-4.4 ± 0.2	CCl_4
11a → **11c**	-0.11 ± 0.02	1.6 ± 0.1	5.8 ± 0.2	CCl_4

[a] At 373 K.

The reaction **12a**→**12b** also involves an isomerization of a β,γ-unsaturated carbonyl compound to the corresponding α,β-isomer but the thermodynamic stability of the system formed is not high, see the modest ΔG°-value of only -2.30 kJ mol^{-1} (Rhoads *et al.*[7] give $\Delta G^{\circ} = -1.57$ kJ mol^{-1}) for this reaction. This result, together with the markedly positive ΔG° values ($\geqq +14$ kJ mol^{-1}) for the **b**→**c** isomerization of **3**–**6** confirms the previous findings[7,9] of the poor thermodynamic stability of a system in which alkoxy and CO groups are disposed *cis* across a C=C bond.

In **2b**, the Me group at C-2 is likely to have a strong negative effect on molecular stability since it forces the MeO group to adopt a high-energy non-s-*cis* conformation, instead of the s-*cis* conformation in **1b**. Yet the thermodynamic stability of **2b** is high enough to cause this isomer to predominate in the equilibrium mixture [K(**b**/**a**) $\geqq$ 100 at 373 K]. On the other hand, in the acyclic ketone **7b** the corresponding Me group lowers the stability of the α,β-isomer sufficiently to produce considerable amounts of the non-conjugated β,γ-isomer (**7a**) in the equilibrium mixture [K(**b**/**a**) = 1.79 at 298.15 K]. The apparently higher destabilizing effect of the Me group concerned on the acyclic ketone **7b** probably follows from a steric repulsion between the Me group and the acetyl moiety, taken to assume the (twisted) s-*cis* conformation. In **2b**, the corresponding steric interaction occurs between the Me group and the carbonyl oxygen and this interaction probably is not repulsive, see the structure of methyl esters of simple carboxylic acids.[17]



In cyclohexane solution, reaction **8a**→**8b** is 5.5 kJ mol^{-1} more exothermic than reaction **7a**→**7b**. This is reasonable since the relative reaction enthalpies might be expected to be determined by the relative steric interaction energies S[Me$\cdots$R] (R = Me for **7b**, R = OMe for **8b**) in the s-*cis* conformation of the reaction products; the relative values of S[Me$\cdots$R] may probably be approximated by the corresponding *cis* interaction energies across a C=C bond, +4.2 kJ mol^{-1} for R = Me (destabilizing) and -2.9 kJ mol^{-1} for R = OMe (stabilizing).[18,19]

The reaction enthalpies for **8a**→**8b**, **10a**→**10b** and **11a**→**11b** are largely determined by the magnitudes of (a) the steric interaction energy between R and the two MeO groups of the ether and ester moieties and (b) the double-bond stabilizing power of the group R. Because of the many contributing factors involved and the uncertainties in their effects on the reaction enthalpy, it is difficult to predict the values of ΔH° (or even their relative order of magnitude) for these reactions. However, the experimental facts show that among the reaction products, **10b** (R = Cl) has the highest thermodynamic stability (relative to the corresponding β,γ-isomer). Similarly, it is even more difficult to predict the values of ΔH° for any reaction involving the other geometric isomer (**c**) since the exact stereochemistry of the acetyl group (in **7c** and **9c**) or the COOMe group (in **8c**, **10c** and **11c**) is not known.

EXPERIMENTAL

Materials. The isomeric forms of **1**–**8** and **10**–**12** were obtained by treatment of the appropriate 1,3-diketones or β-keto esters (e.g. 1,3-cyclohexanedione for **1**, methyl acetoacetate for **4** and methyl 2-chloroacetoacetate for **10**) with trimethyl orthoformate in methanol,[20] usually without isolation of the intermediate acetal. Compound **9** was prepared from 3-chloro-2,4-pentanedione and dimethyl sulfate as described by Verhe *et al.*[21] The yields were moderate to good (30–80%). In the case of **1**–**6**, the presence of only the **b** isomer could be detected (by ^{1}H NMR) in the synthetic products, otherwise a mixture of isomers was obtained. Preparative glc (a Carbowax 20M column) and fractional distillation (Perkin–Elmer M 251 Auto Annular Still) were employed for further fractionation of the isomeric mixtures into their components.

Physical constants. **1** b.p. 99–102°/6 torr, **2** 126–128°/6 torr, **3** 52°/8 torr, **4** 61–62°/7 torr, **5** 65°/8 torr, **6** 82°/20 torr, **7** 50–58°/8 torr (the corresponding acetal, 4,4-dimethoxy-3-methyl-2-pentanone, boiled at 73–75°/15 torr), **8a** 53–55°/6 torr, **8b** (+10% **8c**) 65–70°/6 torr, **9a** 61°/5 torr, **9b** 78°/5 torr, **10a** 78–80°/5 torr, **10b** 104°/5 torr, **10c** *ca.* 86°/5 torr (the acetal boiled at 92°/10 torr), **11** (mainly **11b**) 76–78°/8 torr [the corresponding acetal, methyl 2,3,3-trimethoxy-butanoate, was prepared in 33% yield from methyl 2-chloro-3,3-dimethoxy-butanoate (the acetal used for the preparation of 10) by treatment with NaOMe. The acetal boiled at 89–91°/9 torr], **12a** 93°/11 torr, **12b** 80–81°/2 torr.

^{1}H NMR (60 MHz, CCl_4, Me_4Si, δ values, coupling constants in Hz) and ^{13}C NMR (15 MHz, $CDCl_3$, Me_4Si as internal standard) *spectra.* 3-MeO-2-cyclohexen-1-one (**1b**): ^{1}H NMR 1.7–2.5 ($3CH_2$), 3.63 (MeO), 5.15 (C=CH); ^{13}C NMR 199.6 (C-1), 102.3 (C-2), 178.7 (C-3), 28.9 (C-4), 21.2 (C-5), 36.8 (C-6), 55.5 (MeO). 3-MeO-2-Me-2-cyclohexen-1-one (**2b**): ^{1}H NMR 1.7–2.6 ($3CH_2$), 3.73 (MeO), 1.54 (Me–C=C, t, J = 1.3); ^{13}C NMR 198.7 (C-1), 114.7 (C-2), 172.1 (C-3), 24.8 (C-4), 20.9 (C-5), 36.3 (C-6), 55.2 (MeO), 7.3 (Me–C=C). (*E*)-4-MeO-3-penten-2-one (**3b**): ^{1}H NMR 2.03 (Me–C=C), 2.18 (Me–C=O), 3.57 (MeO), 5.30 (C=CH); ^{13}C NMR 32.0 (C-1), 196.9 (C-2), 99.3 (C-3), 172.7 (C-4), 19.5 (C-5), 55.4 (MeO). Me (*E*) - 3 - MeO - 2 - butenoate (**4b**): ^{1}H NMR 2.26 (Me), 3.61 (MeO), 3.64 (MeO), 4.96 (C=CH); ^{13}C NMR 168.3 (C-1, 90.6 (C-2), 173.2 (C-3), 18.8 (C-4), 55.4 (MeO), 50.7 (COOMe). Et (*E*)-3-MeO-2-butenoate (**5b**): ^{1}H NMR 1.21 (Me–CH_2, t, J = 6.9), 2.19 (Me), 3.53 (MeO), 3.98 (CH_2), 4.82 (C=CH); ^{13}C NMR 167.9 (C-1), 91.0 (C-2), 173.1 (C-3), 18.8 (C-4), 55.4 (MeO), 59.3 (CH_2), 14.4 (Me). t-Bu (*E*)-3-MeO-2-butenoate (**6b**): ^{1}H NMR 1.42 (3Me), 2.19 (Me), 3.57 (MeO), 4.80 (C=CH); ^{13}C NMR 167.4 (C-1), 92.6 (C-2), 172.0 (C-3), 18.6 (C-4), 55.1 (MeO), 78.9 (C quaternary), 28.4 (Me). 4-MeO-3-Me-4-penten-2-one (**7a**): ^{1}H NMR 1.14 (Me, d, J = 6.8), 2.08 (Me–C=O), 3.00 (CH), 3.50 (MeO), 3.92 (CH_2); ^{13}C NMR 27.2 (C-1), 207.5 (C-2), 53.0 (C-3), 163.1 (C-4), 82.7 (C-5), 55.0 (MeO), 14.0 (Me). (*E*)-4-MeO-3-Me-2-penten-2-one (**7b**): ^{1}H NMR 1.78 (Me, q, J = 1.3), 2.06 (Me–C=O), 2.21 (Me, q, J = 1.3), 3.63 (MeO); ^{13}C NMR 30.1 (C-1), 200.8 (C-2), 113.6 (C-3), 163.7 (C-4), 14.7 (C-5), 54.5 (MeO), 12.6 (Me). (*Z*)-4-MeO-3-Me-3-penten-2-one (**7c**): ^{1}H NMR 1.61 (Me, q, J = 1.0), 2.06 (Me–C=C), 2.08 (Me, q, J = 1.0), 3.63 (MeO); ^{13}C NMR 32.5 (C-1), 199.3 (C-2), 115.8 (C-3), 163.0 (C-4), 15.1 (C-5?), 55.1 (MeO), 13.5 (Me?). Me 3-MeO-2-Me-3-butenoate (**8a**): ^{1}H NMR 1.24 (Me, d, J = 7.0), 3.05 (CH), 3.46 (MeO), 3.56 (MeO), 3.88 (CH_2); ^{13}C NMR 173.6 (C-1), 45.2 (C-2), 162.5 (C-3), 81.9 (C-4), 52.0 (COOMe), 55.1 (MeO), 15.4 (Me). Me (*E*)-3-MeO-2-Me-2-butenoate (**8b**): ^{1}H NMR 1.69 (Me, q, J = 1.3), 2.32 (Me, q, J = 1.3), 3.56 (MeO), 3.64 (MeO); ^{13}C NMR 170.1 (C-1), 105.5 (C-2), 165.0 (C-3), 14.5 (C-4), 51.0 (COOMe), 54.8 (MeO), 11.5 (Me). Me (*Z*)-3-MeO-2-Me-2-butenoate (**8c**): ^{1}H NMR 1.86 (Me, q, J = 1.0), 2.32 (Me, q, J = 1.0), 3.52 (MeO), 3.64 (MeO); ^{13}C NMR 174.2 (C-1), 102.4 (C-2), 165.0 (C-3), 17.5 (C-4?), 51.7 (COOMe), 53.2 (MeO), 13.1 (Me). 3-Cl-4-MeO-4-penten-2-one (**9a**): ^{1}H NMR 2.19 (Me–C=O), 3.57 (MeO), 4.18 (C=CH, d, J = 3), 4.35 (C=CH, d, J = 3), 4.50 (CHCl); ^{13}C NMR 25.8 (C-1), 198.8 (C-2), 65.3 (C-3), 157.6 (C-4), 87.3 (C-5), 55.8 (MeO). (*Z*)-3-Cl-4-MeO-3-penten-2-one (**9b**): ^{1}H NMR 2.28 (Me–C=O), 2.40 (Me–C=C), 3.76 (MeO); ^{13}C NMR 30.1 (C-1), 195.5 (C-2), 110.6 (C-3), 163.8 (C-4), 15.1 (C-5), 55.5 (MeO). Me 2-Cl-3-MeO-3-butenoate (**10a**): ^{1}H NMR 3.47 (MeO), 3.61 (MeO), 4.05 (C=CH, d, J = 3), 4.23 (C=CH, d, J = 3), 4.52 (CHCl); ^{13}C NMR 167.2 (C-1), 58.1 (C-2), 157.5 (C-3), 86.7 (C-4), 53.4 (COOMe), 55.9 (MeO). Me (*Z*)-2-Cl-3-MeO-2-butenoate (**10b**): ^{1}H NMR 2.42 (Me–C=C), 3.63 (MeO), 3.75 (MeO); ^{13}C NMR 165.3 (C-1), 102.0 (C-2), 165.1 (C-3), 15.0 (C-4), 52.2 (COOMe), 55.8 (MeO). Me (*E*)-2-Cl-3-MeO-2-butenoate (**10c**): ^{1}H NMR 2.09 (Me–C=C), 3.58 (MeO), 3.61 (MeO); ^{13}C NMR 164.3 (C-1?), 105.4 (C-2), 163.3 (C-3?), 16.1 (C-4), 52.2 (COOMe), 57.3 (MeO). Me 2,3-diMeO-3-butenoate (**11a**): ^{1}H NMR 3.28 (MeO–CH), 3.50 (MeO), 3.67 (MeO), 4.12 (C=CH$_2$), CH not detected; ^{13}C NMR 169.6 (C-1), 81.6 (C-2), 157.7 (C-3), 85.7 (C-4), 53.2 (COOMe), 57.3 (MeO at C-2), 55.3 (MeO at C-3). Me (*E*)-2,3-diMeO-2-butenoate (**11b**): ^{1}H NMR 2.22 (Me–C=C), 3.46 (MeO), 3.67 (MeO), 3.77 (MeO); ^{13}C NMR 166.3 (C-1), 130.4 (C-2), 158.9 (C-3), 14.3 (C-4), 51.3 (COOMe), 60.3 (MeO at C-2), 56.0 (MeO at C-3). Me (*Z*)-2,3-diMeO-2-butenoate (**11c**): ^{1}H NMR 1.96 (Me–C=C), 3.46 (MeO), 3.67 (MeO), 3.77 (MeO); ^{13}C NMR 163.9 (C-1), 131.8 (C-2), 159.8 (C-3), 12.7 (C-4), 52.2 (COOMe), 58.0 (MeO at C-2?), 56.4 (MeO at C-3?). Et 2-MeO-2-cyclopentene-1-carboxylate (**12a**): ^{1}H NMR 1.22 (Me, t, J = 6.9), 1.8–2.5 (2CH$_2$), 3.4 (CH), 3.55 (MeO), 4.05 (CH$_2$O), 4.52 (C=CH); ^{13}C NMR 49.9 (C-1), 96.8 (C-3), 27.8 (C-4), 26.9 (C-5), 174.1 (C=O), 60.9 (CH$_2$O), 14.3 (Me), 57.2 (MeO). Et 2-MeO-1-cyclopentene-1-carboxylate (**12b**): ^{1}H NMR 1.23 (Me, t, J = 6.9), 1.8–2.6 (3 ring CH$_2$), 3.78 (MeO), 4.05 (CH$_2$, q, J = 6.9); ^{13}C NMR 130.8 (C-1), 165.2 (C-2), 31.3 (C-3?), 29.6 (C-4?), 19.2 (C-5?), 169.3 (C=O), 59.1 (CH$_2$O), 14.6 (Me), 57.8 (MeO).

Configurational assignments. The configurations of the geometric isomers of **3**–**6** follow from the configurational assignment of 3 made by Awang[13] and those of **7** and **8** from the magnitude of the homoallylic coupling constant J$_{HH}$ across the C=C bond: in each case, the geometric isomers exhibit J$_{HH}$ values of 1.0 and 1.3 Hz the larger of which should be ascribed to the **b** isomer since the corresponding (*trans*-)homoallylic coupling constant in **2b** is also 1.3 Hz. The more stable geometric isomer of **9** has also been prepared by Verhe *et al.*[21] proposing the structure **b** for it. Finally, the configurations of the geometric isomers of **10** and **11** follow from the remarkable constancy of the ^{13}C NMR chemical shift of the Me group *cis* to the R′CO group in the **b** isomers of **7**, **8** and **9** (δ = 14.7, 14.5 and 15.1, respectively), and hence the observed shift values of 15.0 and 14.3 ppm for the corresponding C atom in the geometric isomers of **10** and **11** should be ascribed to the **b** isomers (rather than the alternative shift values of 16.1 and 12.7 ppm, respectively). In addition, the values of the thermodynamic data of isomerization are easier to comprehend if the configurations of the geometric isomers are taken as proposed by the spectral data.

Equilibrations. The equilibration experiments were carried out in cyclohexane or CCl$_4$ solution with I$_2$ as catalyst.[7,22] The equilibrium mixtures were analyzed by glc (a Hewlett-Packard 5720A gas chromatograph equipped with a Carbowax 20M column) or/and by ^{1}H NMR spectroscopy (a Jeol JNM-PMX60 NMR spectrometer). If the equilibrium mixtures could be analyzed by glc, cyclohexane was used as solvent. In many cases, however, this method was unsatisfactory because of poor separation of the isomeric forms or because of thermal decomposition in the column (**9**–**11**) and then the isomer ratios at equilibrium were determined from the relative integrated intensities of suitable ^{1}H NMR signals from spectra recorded in CCl$_4$ solution. The equilibrium mixtures of **1**–**6** were analyzed by both glc and ^{1}H NMR spectroscopy but the presence of isomers other than the **b** form could not be detected. The equilibrations on **1**–**6** were carried out at 373 K, those on **7** at 257, 276, 293 and 373 K, those on **8**, **10** and **11** at 333, 373 and 403 K, those on **9** at 298, 333, 373 and 403 K, and those on **12** at 297, 333, 373 and 403 K.

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