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Thermodynamics of Vinyl Ethers. XXX.* On the Ease of Introduction of a C=C bond Exocyclic to Some Bi- and Tricyclic Rings

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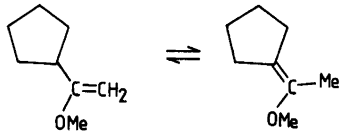
The ease of introduction of a C=C bond exocyclic to a norbornane, norbornene and nortricyclane ring has been studied by chemical equilibration of the isomeric methyl enol ethers of 2-acetylnorbornane, 2-acetylnorbornene and 3-acetylnortricyclane. The process in question is seen to become increasingly more difficult in the sequence norbornane< norbornene<nortricyclane, *i.e.* as the strain in the parent ring system increases. On an enthalpy basis, the introduction of a C=C bond exocyclic to a norbornene ring is *ca.* 2 kJ mol^{-1} less favored, and that to a nortricyclane ring *ca.* 13 kJ mol^{-1} less favored than the introduction of a C=C bond exocyclic to a norbornane ring. Thermodynamic data for other isomerization reactions are also given.

We have previously[1] studied the effect of ring size on the thermodynamics of a reaction in which a C=C bond is transferred from an allylic to an exocyclic position with respect to a carbocyclic ring [see *e.g.* reaction (1)]. As might be expected, the values of the



1a *1b* (1)

thermodynamic parameters of isomerization are markedly affected by ring size. This, of course, is mainly due to variations with ring size in the difference in ring strain energy between a saturated carbocyclic ring (in the reactant) and the corresponding ring containing an exocyclic C=C bond (in the product). In the present work we have applied the same reaction type to study the relative ease of introduction of a C=C bond exocyclic to some bi- and tricyclic ring systems (reactions 2–4). The thermodynamic data of these reactions also give interesting information on the relative stabilities of the geometrical as well as *exo-endo* isomers of these polycyclic compounds.

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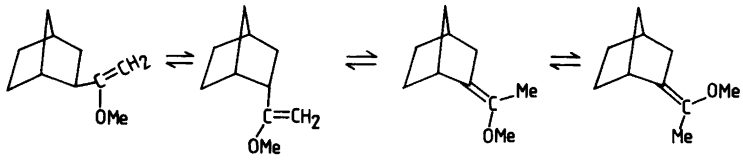
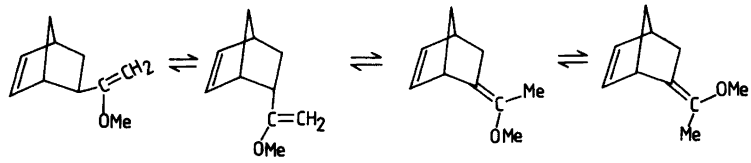


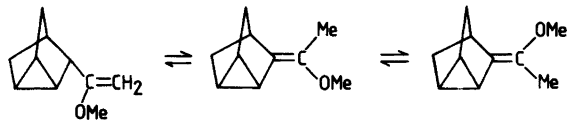
(2)

2a *2b* *2c* *2d*



(3)

3a *3b* *3c* *3d*



(4)

4a *4b* *4c*

EXPERIMENTAL

Materials. The present compounds were prepared by treatment of the appropriate ketones with trimethyl orthoformate in methanol,[2] with or without isolation of the intermediate dimethyl acetal of the ketone used. The yields were 40 to 50 %. Thus, 2-acetylnorbornane gave a roughly equimolar mixture of *2a–2d,* b.p. 72–75 °C/11 Torr, 2-acetylnorbornene similarly a mixture of *3a–3d,* b.p. 73–79 °C/13 Torr, and 3-acetylnortricyclane a mixture of *4a–4c* in the ratio 20:1:1, b.p. 87–88 °C/20 Torr. For compound identification and the equilibrations, pure compounds or mixtures of isomers with sufficiently different compositions were required. These were obtained by fractionation of the crude reaction products with a Perkin-Elmer M 251 Auto Annular Still (only mixtures of isomers could be achieved).

Spectral data. Since the spectra were recorded on mixtures of isomers, not on pure compounds, complete signal assignment failed in many cases. Hence for some compounds only a few characteristic signals are given. *^{1}H NMR spectra* (60 MHz, CCl_4, Me_4Si, δ values): *2a*: 3.72 ($C{=}CH_2$), 3.44 (CH_3O). *2b*: 3.85 ($C{=}CH_2$), 3.38 (CH_3O). *2c*: 3.4 (CH_3O), 1.61 (CH_3). *2d*: 3.4 (CH_3O), 1.75 (CH_3). *3a*: 5.96 (C=CH), 3.76 ($C{=}CH_2$), 3.44 (CH_3O), 2.7 (bridgehead). *3b*: 5.92 (C=CH), 3.63 (C=CH), 3.54 (C=CH), 3.38 (CH_3O), 2.7 (bridgehead). *3c*: 5.9 (C=CH), 3.40 (CH_3O), 2.9 (bridgehead), 1.66 (CH_3). *3d*: 5.9 (C=CH), 3.36 (CH_3O), 2.9 (bridgehead), 1.76 (CH_3). *4a*: 3.80 ($C{=}CH_2$), 3.42 (CH_3O). *4b,4c*: 3.40, 3.44 (CH_3O), 1.76 (CH_3). *^{13}C NMR spectra* (15 MHz, $CDCl_3$, Me_4Si): *2a*: 168.1, 78.4 (olefinic carbons), 54.6 (CH_3). *2b*: 165.8, 80.1 (olefinic carbons), 55.0 (CH_3). *2c*: 141.2, 124.9 (olefinic carbons), 56.6 (CH_3O), 14.3 (CH_3). *2d*: 141.2, 125.5 (olefinic carbons), 55.5 (CH_3O), 14.0 (CH_3). *3a*: 43.2 (C-1), 137.2 (C-2), 136.9 (C-3), 46.6 (C-4), 31.0 (C-5), 46.3 (C-7), 167.5, 79.4 (olefinic carbons of the side chain), 54.7 (CH_3O). *3b*: 42.6 (C-1), 136.3 (C-2), 132.9 (C-3), 45.8 (C-4), 30.4 (C-5), 49.6 (C-7), 166.5, 79.7 (olefinic carbons of the side chain), 54.5 (CH_3O). *3c*: 41.9 (C-1), 134.4 (C-2), 135.7 (C-3), 44.2 (C-4), 121.2 (C-5), 31.5 (C-6), 49.8 (C-7), 142.2 (C-α of the side chain), 56.9 (CH_3O), 15.2 (CH_3). *3d*: 41.9 (C-1), 133.7 (C-2), 135.9 (C-3), 45.9 (C-4), 120.5 (C-5), 30.8 (C-6), 50.1 (C-7), 142.7 (C-α of the side chain), 55.5 (CH_3O), 14.5 (CH_3). *4a*: 10.0, 11.4, 13.2 (cyclopropane

ring carbons), 29.1, 32.4, 34.4 (ring carbons), 48.9 (C-3), 164.7, 80.6 (olefinic carbons), 54.6 (CH_3O). *4b, 4c*: 57.6, 57.0 (CH_3O), 15.4, 14.8 (CH_3).

Structural assignments. Differentation between the *exo* and *endo* forms of *2* (*2a,2b*) and *3* (*3a,3b*) was readily accomplished by comparing their ^{13}C NMR spectra with those of the corresponding isomers of 5-methyl-2-norbornene.[3] On the other hand, configurational assignment of the geometrical isomers was much less straightforward and the assignments proposed here are only tentative. From previous experience with compounds closely related to the present molecules it is known[4,5] that in the systems CH−C=C−CH the values of the homoallylic coupling constant J_{HH} are higher (1.3−1.5 Hz) for the *trans* configuration (although this is not an infallible rule for other types of compounds[6]) while the corresponding *cis* coupling is smaller and may remain unnoticed if the resolution of the spectrometer used is not sufficiently good. In the ^1H NMR spectra of the present compounds the CH_3−C=C groups of the thermodynamically more stable geometrical isomers of *2* and *3* appeared as narrow doublets and those of the less stable geometrical isomers as narrow triplets with the homoallylic coupling constant as *ca.* 1.2 Hz in both cases. From the multiplicities of the signals it can thus be concluded that the former isomers have the structures *2c* and *3c* and the less stable isomers the structures *2d* and *3d*. In the GLC analyses the retention times of *2c* and *3c* were shorter than those of the other geometrical isomers. On this basis we suggest that the shorter of the retention times of the geometrical isomers of *4* should be ascribed to *4c*, in which the bridgehead and the MeO group are *cis* to each other (as in *2c* and *3c*). Of course, this assignment is far from conclusive. From our point of view, however, correct identification of the geometrical isomers is immaterial since in all cases the geometrical isomers appeared to have essentially similar values of the thermodynamic parameters.

Chemical equilibration. The equilibration experiments were carried out in cyclohexane solution with I_2 as catalyst.[7] In each reaction the position of equilibrium was approached from two initial mixtures of isomers. The following mixtures were used: *2*: Mixture A (51.0 % *2a*, 15.2 % *2b*, 17.3 % *2c*, 16.5 % *2d*), mixture B (15.4 % *2a*, 5.9 % *2b*, 40.1 % *2c*, 38.6 % *2d*); *3*: Mixture A (59.9 % *3a*, 19.2 % *3b*, 10.6 % *3c*, 10.3 % *3d*), mixture B (16.8 % *3a*, 20.3 % *3b*, 46.6 % *3c*, 16.2 % *3d*); *4*: Mixture A (100 % *4a*), mixture B (77.8 % *4a*, 12.8 % *4b*, 9.4 % *4c*). The equilibrium mixtures were analyzed by GLC using an XE-60 capillary column for *2* and *4* and a similar packed column for *3*.

RESULTS AND DISCUSSION

The compositions of the equilibrium mixtures at various temperatures are shown in Table 1 and the values of $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$ at 298.15 K for some selected reactions in Table 2.

Table 1. Compositions of the equilibrium mixtures at various temperatures.

Compound No.	*T*/K	*c*(*a*)/%	*c*(*b*)/%	*c*(*c*)/%	*c*(*d*)/%
2	300	35.60	12.77	26.18	25.45
	333	32.57	12.37	27.52	27.53
	373	29.21	11.75	29.81	29.23
	403	27.46	11.45	30.59	30.50
3	298	40.05	25.28	19.83	14.85
	333	36.03	20.77	24.79	18.41
	363	32.90	19.82	26.58	20.71
	393	29.67	19.18	28.52	22.61
	423	28.90	17.60	29.82	23.68
4	299	99.09	0.461	0.448	
	333	98.10	0.968	0.930	
	373	96.43	1.85	1.72	
	403	94.52	2.86	2.63	

Table 2. Values of the thermodynamic parameters $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ at 298.15 K for some selected reactions in cyclohexane solution. The errors are twice the standard errors of a least-squares treatment of ln K against T^{-1}.

Reaction	$\Delta G^{\ominus}$/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}
2a→*2b*	2.551(0.005)	1.46(0.03)	−3.6(0.1)
2a→*2c*	0.81(0.08)	4.2(0.4)	11.3(1.1)
2a→*2d*	0.866(0.010)	4.32(0.06)	11.6(0.2)
2c→*2d*	0.05(0.07)	0.2(0.3)	0.3(1.0)
3a→*3b*	1.24(0.23)	0.2(1.1)	−3.6(3.0)
3a→*3c*	1.64(0.18)	6.1(0.9)	14.9(2.3)
3a→*3d*	2.39(0.18)	6.7(0.8)	14.5(2.3)
3c→*3d*	0.75(0.07)	0.6(0.3)	−0.4(0.9)
4a→*4b*	13.37(0.09)	18.0(0.5)	15.5(1.4)
4a→*4c*	13.42(0.12)	17.4(0.5)	13.2(1.5)
4b→*4c*	0.05(0.03)	−0.6(0.2)	−2.1(0.4)

The latter were evaluated by linear least-squares treatment of ln K against T^{-1}.

The norbornane ring of *2a* may be considered to arise from two "fused" cyclopentane rings. Hence it is of interest to compare the value of $\Delta H^{\ominus}$ for *2a*→*2c*, (4.2±0.4) kJ mol^{-1}, with that for *1a*→*1b*, (1.3±0.1) kJ mol^{-1}.[1] Clearly, more energy is required to introduce an exocyclic C=C bond into a norbornane ring than into a cyclopentane ring. This finding is in agreement with current thermochemical data as shown by the following facts. The standard enthalpy of formation $\Delta H_f^{\ominus}$ of gaseous norbornane, (−52.0±2.3) kJ mol^{-1},[8] suggests a strain energy of *ca.* 58 kJ mol^{-1} for this compound when compared with a calculated $\Delta H_f^{\ominus}$(g) value of −110 kJ mol^{-1}, obtained by using the parameters of the Group method described by Cox and Pilcher.[9] On the other hand, 2-methylenenorbornane is strained by *ca.* 68 kJ mol^{-1} since its $\Delta H_f^{\ominus}$(g) value is calculated to be −30 kJ mol^{-1} while the experimental value appears to be about +38 kJ mol^{-1} (one arrives at this figure by combining the experimental $\Delta H_f^{\ominus}$(l) value of (−4.1±1.6) kJ mol^{-1} with an estimated enthalpy of vaporization value of 42 kJ mol^{-1}, typical for a C_8H_{12} hydrocarbon[8]). Thus the exocyclic methylene group of 2-methylenenorbornane increases the strain by *ca.* 10 kJ mol^{-1}, relative to norbornane. For comparison, 2-methylenecyclopentane is strained by *ca.* 2 kJ mol^{-1}, relative to cyclopentane.[1]

With increasing unsaturation in the reactant the introduction of additional sp^2 hybridized carbons into the ring becomes more difficult, cf. the $\Delta H^{\ominus}$(l) value of 6.1 kJ mol^{-1} for the *3a*→*3c* reaction. This observation is in line with the strain energy values of 58, 74 and 102 kJ mol^{-1}, respectively, for norbornane (no sp^2 carbons), norbornene (two sp^2 carbons) and norbornadiene (four sp^2 carbons).[8,9]

On going to the nortricyclane ring system the difficulty of introducing sp^2 hybridized carbons into the ring is markedly increased as revealed by the value of $\Delta H^{\ominus}$(l), (17.4±0.5) kJ mol^{-1}, for the *4a*→*4c* reaction. Even the reactant *4a* is highly strained: the $\Delta H_f^{\ominus}$(g) value of nortricyclane, (62.0±2.2) kJ mol^{-1},[8] reveals a strain of *ca.* 153 kJ mol^{-1} for this ring system. No doubt most of this strain is due to the presence of the 3-membered ring (the strain of cyclopropane is *ca.* 115 kJ mol^{-1}).[1]

The data of Table 2 show that, at least on a Gibbs energy basis, the *exo* isomers *2a* and *3a* are slightly more stable than the corresponding *endo* forms *2b* and *3b*. For comparison, thermochemical studies show that the *exo* and *endo* forms of 5-methylnorbornene have essentially equal thermochemical stabilities, *cf.* the respective $\Delta H_f^{\ominus}$(l) value of (15.8±0.8)

and (15.8±1.1) kJ mol^{-1}.[8] The *endo* isomers *2b* and *3b* have somewhat smaller entropy values than the corresponding *exo* forms, which probably is a consequence of the apparent steric crowding in the *endo* forms. The entropies of the compounds with an exocyclic C=C bond are considerably higher than those of the other isomers. This is a general trend in these kinds of compounds and it probably arises from a presence of several (at least two) nonplanar gauche rotamers of the MeO group in the exocyclic isomers.[1,7]

The differences in the thermodynamic and thermochemical stabilities of the geometrical isomers involved in this study are small.

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