244. Nucleophilic Addition to C, C-Double Bonds

Part VIII[1])

The Standard Enthalpies of Formation of *anti*^{9,10}-10*endo*-Hydroxytricyclo[4.2.1.1^{2,5}]deca-3,7-dien-9-one and 9-Oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-en-2-one and Kinetic Data for the Cyclization of the Olefinic Alcohol to the Ether

by **Alan A. Smeaton** and **William V. Steele***

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

and **Gerardo M. Ramos Tombo** and **Camille Ganter***

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum,
Universitätsstrasse 16, CH-8092 Zürich

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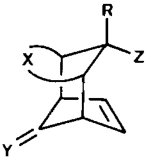
Summary

In view of the significance of steric compression in the base-catalyzed intramolecular cyclization of polycyclic olefinic alcohols, the standard enthalpies of formation of *anti*^{9,10}-10*endo*-hydroxytricyclo[4.2.1.1^{2,5}]deca-3,7-dien-9-one (**1**) and 9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-en-2-one (**2**) as well as the kinetics of the ether formation **1** → **2** were determined.

Introduction. – The structurally enforced close proximity of the reacting centers is the predominant factor for the observed ability of polycyclic olefinic alcohols and amines of type **a** to undergo intramolecular cyclization by nucleophilic attack of the heteroatom on the unactivated C,C-double bond (bearing no electron-attracting groups).



a

R = H or alkyl
X = CH_2-CH_2; $CH_2-CH_2-CH_2$; CH=CH
Y = O; H,H
Z = OH; NH_2

Continuing our studies on the influence of steric compression we have determined the gas-phase standard enthalpies of formation of the olefinic alcohol **1** and the corre-

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[1]) For Part VII, see [1].

sponding ether **2** as well as the kinetics, the activation parameters, and the solvent isotope effect for the selected ether formation **1** → **2**[2]).

Scheme

1

2 R = H

3 R = D

Results. – a) *Thermochemistry.* Results of typical combustion experiments for each compound **1** and **2**[3]) are summarized in *Table 1.* It is impracticable to list details for all experiments, but values of $\Delta U_c^0/M$, the specific energy of the idealized combustion reaction, for all experiments are given in *Table 2.* In each case the combustion reaction is represented by *Equation 1.*

$$C_{10}H_{10}O_2\ (cr) + (23/2)\ O_2\ (g) = 10\ CO_2\ (g) + 5\ H_2O\ (l) \qquad (1)$$

Derived values of the standard molar energy of combustion ΔU_c^0, the standard molar enthalpy of combustion ΔH_c^0, and the standard enthalpy of formation ΔH_f^0, are given in *Table 3* for both compounds **1** and **2** in the condensed state. The uncertainties

Table 1. *Summary of Typical Calorimetric Experiments at 298.15 K.* The symbols and abbreviations are those of [4] except as noted.

Compound	m (compound) [g]	m (cotton) [g]	ΔR [Ω]	$-\Delta R\varepsilon$ (calor)[a]) [kJ]	$-\Delta R\varepsilon$ (cont) [kJ]	ΔU_w[b]) [kJ]	ΔU (ign) [kJ]	$-\Delta u_c^0$(compound) [kJ · g^{-1}]
1	0.051741	0.001046	1.79532	1.6717	0.0052	0.0011	0.0015	32.0303
2	0.055081	0.001565	1.89062	1.7604	0.0054	0.0011	0.0011	31.5569

[a]) ε (calor) denotes the energy equivalent of the calorimeter: (931.12 ± 0.35) J · Ω^{-1}.

[b]) Items 81–85, 87–90, 93, and 94 of the computational form of ref. [5], correction to standard states.

Table 2. *Summary of Experimental Results at 298.15 K*

Compound	$-\Delta u_c^0$(compound) [kJ · g^{-1}]	$-\Delta u_c^0$(compound) [kJ · g^{-1}]	Mean	Standard deviation
1	32.0385	32.0048	32.0238	0.0077
	32.0058	32.0303		
	32.0394			
2	31.5490	31.5572	31.5559	0.0024
	31.5605	31.5569		

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[2]) For qualitative studies on the reaction **1** → **2** see [2].

[3]) For earlier determinations of the standard enthalpies of formation of bridged ring molecules, see [3] and ref. cit. therein.

Table 3. *Derived Molar Values for the Condensed State at 298.15 K*

Compound	$-\Delta U_c^0$ [kJ · mol^{-1}]	$-\Delta H_c^0$ [kJ · mol^{-1}]	$-\Delta H_f^0$ [kJ · mol^{-1}]
1	5193.91 ± 3.0	5197.6 ± 3.0	166.65 ± 3.0
2	5118.02 ± 1.2	5121.74 ± 1.2	242.5 ± 1.5

attributed to the final results in *Table 3* are twice the standard error of the mean and include the uncertainties in the calibrations and subsidiary experiments. Using the values [6] $\Delta H_f^0(CO_2, g) = -393.51$ kJ · mol^{-1} and $\Delta H_f^0(H_2O, l) = -285.83$ kJ · mol^{-1}, we calculate the following standard enthalpies of formation: $\Delta H_f^0(C_{10}H_{10}O_2$, alcohol **1**, cr$) = -(166.65 \pm 3.0)$ kJ · mol^{-1} and $\Delta H_f^0(C_{10}H_{10}O_2$, ether **2**, cr$) = -(242.5 \pm 1.5)$ kJ · mol^{-1}.

The standard molar enthalpies of sublimation of the alcohol **1** and the ether **2** were obtained by fitting the values in *Table 8* (see *Exper. Part*) by least squares to

$$R \cdot \ln(p/[\mathrm{Pa}]) = -\Delta G_{\mathrm{sub}}^0/\theta + \Delta H_{\mathrm{sub}}^0(\theta^{-1} - T^{-1}) \qquad (2)$$

where θ is 298.15 K and $\Delta G_{\mathrm{sub}}^0$ and $\Delta H_{\mathrm{sub}}^0$ are the standard molar *Gibbs* energy and the molar enthalpy of sublimation at temperature θ. *Equation 2* is a simplified version of the equation derived in reference [7]. The results are summarized in *Table 4*.

Table 5 lists the calculated and observed gas-phase enthalpies of formation for both the alcohol **1** and the ether **2**. The calculated values were obtained using the MM2 modification of the alcohol force-field of *Allinger & Chung* [8].

b) *Kinetics.* The reaction rate for the cyclization **1** → **2** in *t*-BuOK/*t*-BuOH was measured in the temperature range of 20–80 °C and the activation parameters calculated thereof applying the *Arrhenius* relation by means of linear regression. The solvent

Table 4. *Standard Molar* Gibbs *Energies and Molar Enthalpies of Sublimation at 298.15 K*

Compound	$\Delta G_{\mathrm{sub}}^0$ [kJ · mol^{-1}]	$\Delta H_{\mathrm{sub}}^0$ [kJ · mol^{-1}]
1	5.97	(103.0 ± 1.5)
2	5.26	(96.0 ± 1.5)

Table 5. *Calculated and Observed Standard Molar Enthalpies of Formation*

Compound	ΔH_f^0 (g) [kJ · mol^{-1}]	
	calculated	observed
1	− 61.9	−(63.65 ± 3.4)
2	−145.2	−(146.5 ± 2.1)

Table 6. *Kinetic Data for the Reaction* **1** → **2** *in* t-*BuOK*/t-*BuOH*

k_B (at 20.5°) [s^{-1} · mol^{-1} · kg]	k_{ROH}/k_{ROD} (at 30°)	E_a[a]) [kJ · mol^{-1}]	A[a]) [s^{-1}]	$\Delta H^{\neq}$[b]) [kJ · mol^{-1}]	$\Delta S^{\neq}$[b]) [J · K^{-1} · mol^{-1}]	$\Delta G^{\neq}$[b]) [kJ · mol^{-1}]
$2.2 \pm 0.3 \cdot 10^{-3}$	1.7	108.4	$5.5 \cdot 10^{16}$	105.9	67.4	86.2

[a]) Correlation: 0.959.

[b]) Calculated from E_a and A according to [9].

isotope effect k_{ROH}/k_{ROD} was measured in *t*-BuOK/*t*-BuOH and *t*-BuOK/*t*-BuOD, respectively. The results are listed in *Table 6*.

Discussion. – The cyclization **1** → **2** implies a nucleophilic attack of an alkoxide anion on an isolated C,C-double bond and is an example for the observed base-catalyzed ether formation in polycyclic alcohols of type **a** (Z = OH).

Steric compression alone (**a**, Y = H,H) or in combination with electronic effects (**a**, Y = O) is responsible for this uncommon reactivity. Increasing the steric compression in olefinic alcohols (**a**, R = CH_3 *vs.* R = H and/or X = CH_2CH_2 *vs.* X = $CH_2CH_2CH_2$) always enhances significantly the reaction rate[4]. For the ether formation **1** → **2** both, proximity and homoconjugative effects are the driving forces [2].

The observed Δ (ΔH_f^0)-values for the alcohol **1** and the ether **2** for the gas and the solid phase are very similar (−82.85 and −75.85 kJ · mol^{-1}, respectively) and can, at least in part, be correlated with the strain release upon cyclization.

The reaction **1** → **2** exhibits second-order kinetics (first-order with respect to the alcohol **1** as well as to the base) and a half-life time of *ca.* 5 min at room temperature in 1 molal *t*-BuOK/*t*-BuOH. The addition of the OH group on the C,C-double bond occurs stereoselectively as shown by an experiment in *t*-BuOK/*t*-BuOD (→ **3**): one D-atom is incorporated at C(11) from the *exo*-side.

The small solvent isotope effect k_{ROH}/k_{ROD} = 1.7 (in *t*-BuOK/*t*-BuOH and *t*-BuOK/*t*-BuOD, respectively, at 30°) together with the positive value of $\Delta S^{\neq}$ (67.4 J · K^{-1} · mol^{-1}) are compatible with an addition mechanism formally corresponding to the reverse of a E_1cB elimination [10].

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Experimental Part

General. Compounds **1**–**3** are described in [2]. For thermochemical measurements, **1** and **2** were purified by column chromatography on silica gel in cyclohexane/AcOEt 1:1 and pentane/Et_2O 1:1, respectively, followed by sublimation: **1** at 65°/10^{-3} Torr and **2** at 60°/10^{-3} Torr.

Thermochemistry. The bomb calorimeter (internal volume 0.021 dm^3), its calibration, and the auxiliary equipment will be described [11]. It has previously been used in a thermochemical study of tri(*tert*-butyl)methanol [12]. The calorimeter was calibrated using 0.06 cm^3 of H_2O initially in the bomb and an internal O_2 pressure of 3.0 MPa at 298.15 K. The bomb was flushed with O_2 before charging to the stated pressure. The standard energy of combustion and empirical formula of the cotton fuse were 16.240 kJ · g^{-1} and $CH_{1.8}O_{0.9}$, respectively.

The experimental results are based on 1975 atomic weights [13]. For reducing weighings in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states [5], the values in *Table 7* were used for the density ρ, specific heat capacity c_p, and $(\delta u/\delta p)_T$. All densities were experimentally determined. Heat capacities were measured on the d.s.c. using sapphire as a standard [14]. All other values of physical properties are estimates.

The combustion products were examined for CO (*Winkler*'s reagent) and unburnt C, but neither was detected. No HNO_3 or HNO_2 were formed during the series of combustions [15].

The torsion-effusion and mass-loss-effusion apparatus used for vapour-pressure measurements in the tri(*tert*-butyl)methanol work [12] has been used here to determine the temperature dependence of the vapour

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[4] Detailed kinetic studies about the influence of steric compression and homoconjugative effects on the cyclization rates for compounds of type **a** are subject of a forthcoming paper.

Table 7. *Physical Properties at 298.15 K.* Values in parentheses are estimates.

Compound	M [$g \cdot mol^{-1}$]	ρ [$g \cdot cm^{-3}$]	$-(\delta u/\delta p)_T$ [$J \cdot g^{-1} \cdot kPa^{-1}$]	c_p [$J \cdot g^{-1} \cdot K^{-1}$]
Cotton	28.22	1.5	negligible	1.67
1	162.189	1.35	(0.003)	1.42
2	162.189	1.4	(0.003)	1.32

Table 8. *Variation of Vapour Pressure with Temperatur*

Alcohol **1**:	T [K]	294.0	298.5	307.0	310.3	312.4
	p [Pa]	0.05	0.09	0.30	0.47	0.59
Ether **2**:	T [K]	295.0	298.0	305.0	307.0	310.0
	p [Pa]	0.08	0.12	0.29	0.36	0.54

pressure of both the alcohol **1** and the ether **2**. Collision diameters of 700 pm (**1**) and 650 pm (**2**) were used in the calculation of the vapour pressures.

The calculated values of p (torsion) and p (mass loss) agreed well (ratio: 1.00 ± 0.03 in both cases) assuming a monomeric molar mass for the effusing molecules. *Table 8* gives a representative set of calculated pressures and their corresponding temperatures for both the alcohol **1** and the ether **2**.

Kinetics. A *ca.* 1:1 mixture of **1** and naphthalene as internal standard was dissolved (*ca.* 0.1 mmol/ml) under Ar in abs. *t*-BuOH and thermostated in a water bath. The reaction was started by injection of a thermostated *t*-BuOK/*t*-BuOH solution. The samples were taken every 3 min, quenched with ice/H_2O and extracted with pentane. The org. layer was analyzed by capillary GLC using a *Carlo-Erba Fractovap 4160* gas chromatograph equipped with a *UCON 50 HB 5100* glass capillary column (25 m/0.33 mm) and a *Hewlett-Packard 3390 A* integrator. The extraction and analysis procedure was calibrated (error limit $< \pm 1\%$) by using mixtures of **1**, **2**, and naphthalene of known compositions.

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