J. Am. Chem. Soc. **2000,** *122,* 3033−3036

The 2-Vinylphosphirane−3-Phospholene Rearrangement: Biradicaloid and Concerted Features

Maurice J. van Eis, Tom Nijbacker, Franciscus J. J. de Kanter, Willem H. de Wolf, Koop Lammertsma,* and Friedrich Bickelhaupt*

Contribution from the Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV, Amsterdam, The Netherlands

Received October 27, 1999

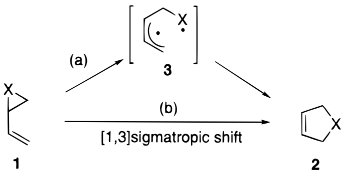
Abstract: Activation parameters have been determined for the 2-vinylphosphirane−3-phospholene rearrangement in the cycloheptane annellated series **7** → **8**. For the thermal reaction, the mean activation parameters ($\Delta H^\ddagger = 125 \pm 5$ kJ mol^{-1} and $\Delta S^\ddagger = -1 \pm 14$ J K^{-1} mol^{-1}) are as expected for a biradicaloid character of the transition structure. In the presence of Cu(I) as a catalyst, the activation parameters for this conversion ($\Delta H^\ddagger = 80.2 \pm 3$ kJ mol^{-1} and $\Delta S^\ddagger = -100 \pm 7$ J K^{-1} mol^{-1}) are strikingly different and more in line with a concerted pathway.

Introduction

Since its discovery nearly 4 decades ago,[1] the structural rearrangement of vinylcyclopropane (**1a**) to cyclopentene (**2a**) has been subject to controversy.[2] Two limiting pathways have been proposed: (a) a rearrangement involving a biradical intermediate **3a** and (b) a concerted [1,3] sigmatropic shift (Scheme 1).

Interestingly, the reaction shows characteristics of both. There is ample evidence for the involvement of a biradical.[3] However, the rearrangement of, e.g., a *tert*-butyl substituted vinylcyclopropane proceeds with high stereospecificity under inversion at the migrating carbon in support of a Woodward−Hoffmann allowed suprafacial [1,3] sigmatropic shift.[4] Recent studies[5] suggest that these seemingly contradictory results may be reconciled by recognizing that the transition state structure lies on a rather flat plateau and has considerable biradical character, with dynamic effects playing a decisive role in the stereochemical course of the reaction.

Scheme 1[a]



[a] **a**: X = CH$_2$. **b**: X = RP. **c**: X = PhPW(CO)$_5$.

Surprisingly, the related vinylphosphirane−phospholene rearrangement has received little attention. On the basis of an exploratory kinetic study, Richter proposed that the thermal rearrangement of 1-*tert*-butyl-2-vinylphosphirane (**1b**, R = *t*-Bu) occurs via a biradical intermediate.[6] Mathey et al.[7] reported the addition of terminal phosphinidene complex PhPW(CO)$_5$ (**4**) to 1,3-butadiene to give a 2-vinylphosphirane complex of type **1c**, which rearranges to the corresponding 3-phospholene (**2c**), but stereochemical details were not provided. Lammertsma et al.[8] studied the addition of **4** to cyclic dienes and reported a vinylphosphirane−phospholene rearrangement with inversion at the phosphorus center but provided no kinetic data. Recently, we observed the formation of phospholenes both by a direct 1,4-addition of **4** to cisoid 1,3-dienes and by a stepwise process via the corresponding 1,2-adducts.[9] In the present study we report on the kinetics of this latter conversion, i.e., the rearrangement of a vinylphosphirane to the (formal) 1,4-adduct, a phospholene.

Results and Discussion

Reaction of 1,2-dimethylenecycloheptane (**6**) with **4**, generated by the CuCl-catalyzed cheletropic elimination from **5** at 50 °C in xylene, affords a mixture of 1,2-adducts **7a** and **7b** and 1,4-adduct **8** in 53, 28, and 19% yield, respectively (Scheme 2).[9] Heating to 100 °C converts both vinylphosphiranes **7a,b** to phospholene **8**; the latter was characterized by an X-ray crystal structure determination.[9] The 1,2-adducts **7a,b** could not be isolated separately, but were identified in the mixture by ^{31}P NMR spectroscopy.

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(4) For experiments in favor of a concerted mechanism see: (a) Gajewski, J. J.; Olson, L. P. *J. Am. Chem. Soc.* **1991**, *113*, 7432. (b) Gajewski, J. J.; Olson, L. P.; Willcott, M. R., III *J. Am. Chem. Soc.* **1996**, *118*, 299.

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10.1021/ja993829q CCC: $19.00

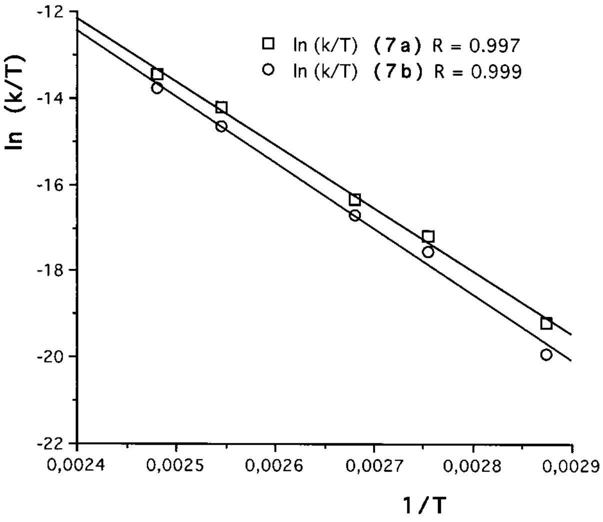

Figure 1. Eyring Plot for the uncatalyzed thermal rearrangement of **7** to **8**. Squares and circles represent the data from Table 1 for **7a** and **7b**, respectively. The straight lines are unweighted linear regressions.

Scheme 2

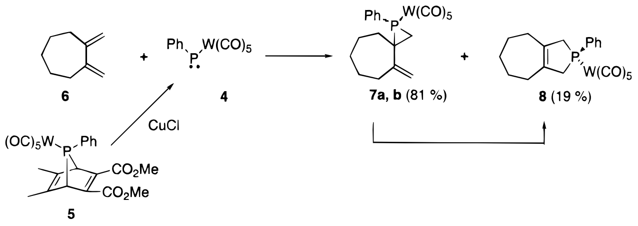

Table 1. Kinetic Data for the Thermal Rearrangement of **7** to **8**

entry	T (K)	10^6k (**7a**) (s^{-1})	10^6k (**7b**) (s^{-1})
1	403.0	428.1 ± 6.4	594.8 ± 14.8
2	393.0	167.4 ± 3.2	271.2 ± 8.6
3	373.0	20.7 ± 0.45	29.67 ± 1.36
4	363.0	8.62 ± 0.32	12.49 ± 0.54
5	348.0	0.77 ± 0.09	1.62 ± 0.06

The mixtures of **7a**,**b** and **8** employed in the present study were freshly prepared from **5** and **6** and carefully purified by TLC (2−3 times) to completely remove CuCl. We determined rate constants k for the conversion of **7a**,**b** to **8** at 75−130 °C in 10−15 deg intervals by monitoring the disappearance of their ^{31}P NMR chemical shifts at δ −136.1 and −132.3 ppm. Excellent mass recovery of >90% was observed for all conversions. First-order kinetics was confirmed by the linear relationship between ln([**7**]) and time (t). Interestingly, the reaction rates are slightly different for **7a** and **7b**. Each isomer gives a good linear relationship between ln(k/T) and 1/T [**7a**, R = 0.997; **7b**, R = 0.999] (Figure 1). The activation parameters for the rearrangement **7a** → **8** are $\Delta H^{\ddagger} = 127.4 \pm 6.0$ kJ mol^{-1} and $\Delta S^{\ddagger} = 5.0 \pm 16.0$ J K^{-1} mol^{-1} (Arrhenius parameters (T = 373 K): $E_a = 130.5 \pm 6.1$ kJ mol^{-1} and ln $A = 31.3 \pm 1.9$). For the process **7b** → **8**, these values are $\Delta H^{\ddagger} = 121.6 \pm 3.6$ kJ mol^{-1} and $\Delta S^{\ddagger} = -6.8 \pm 9.6$ J K^{-1} mol^{-1} (Arrhenius parameters (T = 373 K): $E_a = 124.8 \pm 3.7$ kJ mol^{-1} and ln $A = 29.9 \pm 1.2$). The average values for **7** → **8** are $\Delta H^{\ddagger}_{av} = 125 \pm 5$ kJ mol^{-1} and $\Delta S^{\ddagger}_{av} = -1 \pm 14$ J K^{-1} mol^{-1}.

Even though the activation enthalpies are considerably smaller than those for the analogous vinylcyclopropane−cyclopentene rearrangement (216 kJ mol^{-1}),[10] they are in line with expectations for a biradicaloid pathway. A limiting $\Delta H^{\ddagger}$ value for such a pathway can be deduced as follows. Homolytic cleavage of a P−C bond is estimated at 264 kJ mol^{-1}.[11] Stabilization of the resulting biradical by allylic resonance is estimated at 63 kJ mol^{-1}.[12] Strain relief of the phosphirane further reduces $\Delta H^{\ddagger}$; for the parent C_2H_5P system, a ring strain of 84 kJ mol^{-1} was found at G2 theory.[13] Combining these energies gives $\Delta H^{\ddagger} = 117$ kJ mol^{-1} for generating biradical intermediate **3b** from **1b** (R = H). This estimate does, of course, not consider the effect of W(CO)$_5$ complexation on the P−C bond strength, on the phosphirane ring strain, or on the resonance stabilization of the biradical.[13] Moreover, it is reasonable to assume that the allylic delocalization is not yet fully developed in the transition state and that the ring strain has not been released completely. For example, based on kinetic data, it was suggested that the transition state for the vinylcyclopropane−cyclopentene rearrangement retains 21 kJ mol^{-1} of ring and torsional strain.[10c] Therefore, one may conclude that the actual activation enthalpy for the formation of biradical **3c** is higher than the 117 kJ mol^{-1} mentioned above; indeed, this is what we find, and the differences are seductively small (**7a** → **8**, $\Delta\Delta H^{\ddagger} = 10.4$ kJ mol^{-1}; **7b** → **8**, $\Delta\Delta H^{\ddagger} = 4.6$ kJ mol^{-1}). The low activation entropies of 5.0 ± 16.0 (**7a**) and −6.8 ± 9.6 J K^{-1} mol^{-1} (**7b**) are also in line with a biradicaloid transition structure. A similarly low $\Delta S^{\ddagger} = 6 \pm 5$ J K^{-1} mol^{-1} has been reported for the rearrangement of 1-alkoxy-1-vinylcyclopropane to the corresponding 1-alkoxycyclopentene.[14] It was suggested to follow a biradicaloid pathway; the relatively small value of $\Delta S^{\ddagger}$ was attributed to cancellation of positive contributions (cyclopropane ring opening) and negative ones (hindered rotation of the allyl radical).[14] Analogous entropy effects may be expected for a biradicaloid rearrangement **7** → **8**.

Conducting the vinylphosphirane rearrangement in the presence of the N-*tert*-butylphenylnitrone spin trap gave no detectable amounts of radicals. This testifies to the at best fleeting existence[2b,5g,15] of a biradical intermediate such as **3**.

Thus it appears that the thermal vinylphosphirane−phospholene rearrangement **7** → **8** has kinetic parameters which place it more at the biradicaloid end of the flat mechanistic plateau that is well-known for the vinylcyclopropane−cyclopentane rearrangement.

During this investigation, we found the rearrangement to proceed markedly faster in crude reaction mixtures, presumably due to the presence of traces of CuCl. Again, the disappearance of **7** followed first-order kinetics, but the reproducibility for different runs was somewhat less satisfactory than that for the uncatalyzed reaction because of presumed decomposition (^{31}P NMR: 10−20%, especially in the higher temperature range). Interestingly, the reaction rates for the conversion to **8** are the same for **7a** and **7b** within the limits of detection over the temperature domain of 50−100 °C (Table 2). As a result, the ratio of **7a** and **7b** remains constant and the linear relationship between ln(k/T) and 1/T is essentially identical for both isomers [$R = 0.998$] (Figure 2).

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Table 2. Kinetic Data for the Cu(I)-Catalyzed Thermal Rearrangement of **7** to **8**

entry	T (K)	10^6k (**7a**) (s^{-1})	10^6k (**7b**) (s^{-1})
1	373.0	305 ± 17	303 ± 48
2	353.0	56.3 ± 0.2	59.7 ± 4.3
3	342.4	26.1 ± 1.3	24.5 ± 2.2
4	332.8	11.8 ± 1.5	13.5 ± 1.5
5	323	4.6 ± 0.4	4.3 ± 0.4

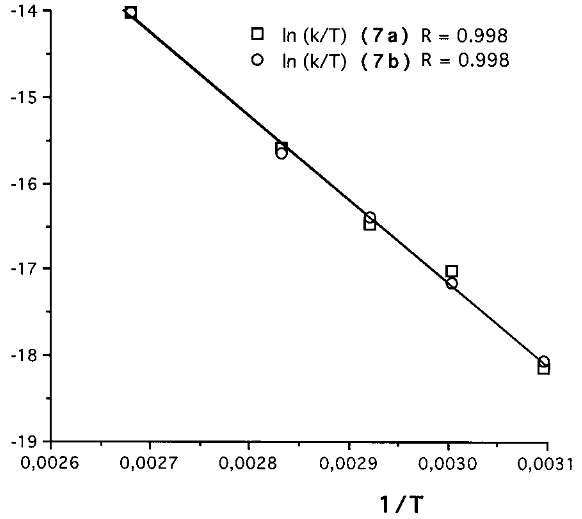

Figure 2. Eyring Plot for the CuCl-catalyzed thermal rearrangement of **7** to **8**. Squares and circles represent the data from Table 2 for **7a** and **7b**, respectively. The straight line is an unweighted linear regression.

The activation parameters for the CuCl catalyzed rearrangement **7** → **8** are $\Delta H^{\ddagger} = 80.2 \pm 2.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -100 \pm 7$ J K^{-1} mol^{-1} (Arrhenius parameters ($T = 373$ K): $E_a = 83.9 \pm 3.1$ kJ mol^{-1} and ln $A = 18.9 \pm 0.9$). The activation enthalpy of 80 kJ mol^{-1} is significantly lower than that for the uncatalyzed biradicaloid reaction for **7a** (127 kJ mol^{-1}) and **7b** (122 kJ mol^{-1}). This fact as well as the strongly negative activation entropy of −100 J $K^{-1}mol^{-1}$ point to a higher degree of concertedness of this reaction which must be attributed to the presence of CuCl. The transition-metal (Ni^0, Pd^0) catalyzed rearrangement of substituted 2-vinylphosphiranes reported by Richter[6b,c] may be considered as a precedent for such a transformation. While the role of copper(I) as a catalyst remains to be elucidated, we speculate that initially, Cu(I) coordinates to the double bond[16] of **7** and subsequently stabilizes the transition structure while shifting it toward the concerted end of the mechanistic spectrum. However, it must be pointed out that the ^{1}H NMR spectrum of **7** remains unchanged upon addition of CuCl; therefore the initial activating copper complex must be present in a low concentration beyond the detection limit of 1%. We consider cleavage of the C−P bond by Cu(I) to form a four-membered metallacycle[17] prior to rearrangement to **8** a less likely alternative.

Conclusions

The kinetic data for the thermal rearrangement of the $W(CO)_5$ complexed vinylphosphirane **7** to the corresponding phospholene **8** ($\Delta H^{\ddagger}_{av} = 125$ kJ mol^{-1} and $\Delta S^{\ddagger}_{av} = -1$ J K^{-1} mol^{-1}) suggest a mechanism with biradicaloid features, in line with the analogous vinylcyclopropane rearrangement. Interestingly, the rearrangement is catalyzed by CuCl, and according to the activation parameters ($\Delta H^{\ddagger} = 80$ kJ mol^{-1} and $\Delta S^{\ddagger} = -100$ J K^{-1} mol^{-1}), this apparently shifts the mechanism toward a concerted process.

Experimental Section

General Procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker MSL 400 spectrometer at 400.13, 100.62, and 162.0 MHz, respectively. ^{1}H NMR spectra were referenced to $CHCl_3$ (δ 7.27 ppm), ^{13}C NMR spectra to $CDCl_3$ (δ 77.0 ppm), and ^{31}P NMR spectra to external H_3PO_4. High-resolution mass spectrometry (HRMS) was performed on a Finnigan MAT-90 mass spectrometer operating at an ionization potential of 70 eV. Melting points were measured on samples in unsealed capillary tubes and are uncorrected. Microanalyses were performed by Microanalytisches Labor Pascher. Xylene (mixture of isomers) and toluene were purchased from Aldrich, distilled from sodium, and stored on sodium under nitrogen. CuCl (99.99% purity) was purchased from Acros and stored under nitrogen. Preparative thick-layer chromatography was carried out on alumina plates. Diene **6**[18] and **7a**, **7b**, and **8** were prepared as described previously;[9] **7a** and **7b** were obtained as an inseparable mixture with the corresponding 1,4-adduct **8**, and have not been isolated.[9] Their identity is based on ^{31}P NMR spectroscopy and on their (close to) quantitative conversion to **8**.

Kinetic Measurements. (a) Uncatalyzed Rearrangement. Double and more runs were performed with slightly different amounts of starting materials **7a**,**b** and **8** which were obtained in several preparations. In all cases, identical k values were obtained. A representative experiment is described below.

In a one-necked flask, **5** (243 mg, 0.37 mmol) and CuCl (5 mg) were 3 times evacuated and flushed with nitrogen. Then toluene (3 mL) and **6** (74 mg, 0.6 mmol) were added and the mixture was stirred under nitrogen for about 30 h at 23 °C. At this stage, ^{31}P NMR revealed the presence of a mixture of **7a**,**b**, and **8** in a ratio of approximately 2:1:1. The reaction mixture was concentrated at reduced pressure and the residue was purified by column chromatography (Al_2O_3/pentane) to afford a yellow oil. Further purification was achieved by repetitive TLC (Al_2O_3/pentane) (2−3 times) to yield a pale yellow oil consisting of **7a**, **7b**, and **8** in a 2:1:1 ratio. Yield: 137 mg (0.25 mmol, 67%).

In an NMR tube, 10−20 mg samples of this mixture were dissolved in 0.50 mL of dry toluene under nitrogen. After tightly capping the NMR tube with a Teflon cap, the conversion of **7a** and **7b** to **8** was monitored by ^{31}P NMR spectra which were acquired at 20−60 min intervals depending on the temperature at which the reaction was performed. Normally 10−30 data points were collected. The ^{31}P NMR spectra were recorded separately (**7a** + **7b**; **8**) and successively in unlocked mode with a SW of 4000 Hz and decoupling only during aquisition. Multipulse decoupling with WALTZ-16 has been applied to suppress heating effects during acquisition. In each case, 32 transients were acquired over 5 min (pulse repetition time 9.5 s, acquisition time 2.05 s, relaxation delay 7.5 s). After careful phasing of the signals, their areas were accurately integrated. The temperature of the NMR probe was calibrated using the standard ethylene glycol method of Geet before acquisition.[19] Temperatures were shown to vary by no more than 0.1 °C during the course of each experiment, but the accuracy is assumed to be not better than ±1 °C.

The rearrangement of **7** was studied at five temperatures in the range from 75 to 130 °C. First-order graphs were obtained by plotting the natural logarithm of the integrals, ln([**7**]), vs time (t). Rate constants were obtained from the slope of the linear regression line to the experimental data using a 95% confidence level with errors of approximately 2 standard deviations (Table 1).

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The Eyring plots (ln(k/T) vs 1/*T*) are shown in Figure 1. Activation parameters were obtained by a linear least-squares fit to the data: (**7a** → **8**) $\Delta H^{\ddagger} = 127.4 \pm 6.0$ kJ mol^{-1} and $\Delta S^{\ddagger} = 5.0 \pm 16.0$ J K^{-1} mol^{-1}; (**7b** → **8**) $\Delta H^{\ddagger} = 121.6 \pm 3.6$ kJ mol^{-1} and $\Delta S^{\ddagger} = -6.8 \pm 9.6$ J K^{-1} mol^{-1}. Errors are 95% confidence regions and correspond to 2 standard deviations.

(b) Copper-Catalyzed Rearrangement. Solutions containing a mixture of **7a**, **7b**, and **8** in a 2:1:1 ratio were freshly prepared as follows. In a 5 mm NMR tube (507 pp), **5** (39.49 mg, 0.060 mmol), **6** (14.64 mg, 0.012 mmol), CuCl (5−6 mg, about 10 mol % of **5**), and xylene (0.5 mL) were introduced. The NMR tube was flushed with nitrogen and capped. After wrapping the cap with Teflon tape, the tube was transferred to the preheated NMR probe. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After the starting material **5** had disappeared (approximately 10 h), the conversion of **7a** and **7b** to **8** was monitored by ^{31}P NMR spectroscopy. For additional details see the uncatalyzed reactions.

The rearrangement of **7** was studied at five temperatures in the range from 50 to 100 °C. Rate constants (Table 2) and Eyring plots (Figure 2) were obtained as described for the uncatalyzed rearrangement giving $\Delta H^{\ddagger} = 80.2 \pm 2.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -100 \pm 7$ J K^{-1} mol^{-1}.

Acknowledgment. We thank Dr. H. Zappey for performing the HRMS measurements. This investigation was supported by the Council of Chemical Sciences (GCW) with financial aid from The Netherlands Organization for Scientific Research (NWO).

JA993829Q