252. On the Mechanism of the α-Alkynone Cyclization: A Theoretical Study

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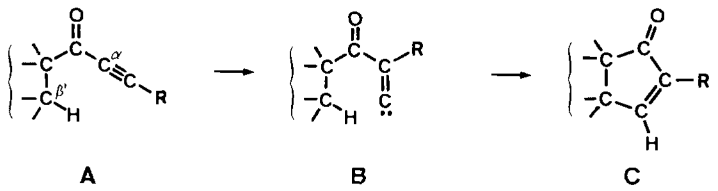
Summary

The acetylene→carbene rearrangement of three model α-alkynones, namely propynal (**1a**), 2-butynal (**1b**) and butynone (**1c**) is studied by *ab initio* double-zeta, double-zeta plus polarization and double-zeta plus self-consistent electron pairs calculations. Transition states are located by force-gradient geometry optimization. Calculated minimum energy reaction paths reveal substituent effects on the activation parameters, which indicate that a H-atom or an alkyl group competes favorably with an acyl group in the [1,2]-shift from α-alkynones **1** to the corresponding acylvinylidenes **5**.

1. Introduction. – The α-alkynone cyclization [1] is a thermochemical isomerization of ethyl ethynyl ketones **A** to 2-cyclopentenones **C**. A plausible mechanism is the [1,2]-shift of one of the substituents at the acetylenic C-atoms leading to a carbene intermediate **B**, which subsequently undergoes an insertion into the aliphatic H, C(β')-bond *(Scheme 1)*.

Scheme 1



The rate-determining step of this reaction is most likely the [1,2]-shift **A**→**B**, since carbenes usually 'insert' into C, H-bonds without – or almost without – activation energy [2]. The question that cannot be answered immediately either on the basis of the available experimental data or on the basis of chemical intuition is

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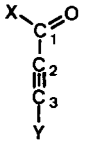
which of the two acetylenic substituents in **A** actually does migrate, the acyl group or the substituent R (H-atom or alkyl group).

[1,2]-Hydrogen shifts involving carbenes have been studied by a number of authors with the aid of qualitative [3], semiempirical [2] and nonempirical [4–6] theoretical methods. It is now well-recognized that a reliable study of reaction paths involving intermediates of low stability requires precise descriptions of the transition state geometries and energies. Qualitative theories or semiempirical quantum chemical methods appear not to be adequate in the case of carbene [1,2]-shifts. MINDO/2, for example, predicts no activation energy for the rearrangement of methylcarbene to ethylene [2]; methyl carbene is even a local maximum of the MINDO/2 potential surface. Nonempirical calculations, on the other hand, predict sizable barriers separating carbenes and isomeric octet hydrocarbens [4–6]. For this reason we used nonempirical MO-calculations of the total energy and the molecular geometry along the reaction coordinate of the above-mentioned [1,2]-shifts **A** → **B**.

2. Methodological details. – The following model molecules were studied in this work: propynal (**1a**), 2-butynal (**1b**) and butynone (**1c**). The answer to the above-stated question was expected to be obtained by comparison of calculated energy differences (activation energies) for the following pairs of competing shifts: hydrogen *vs.* formyl, methyl *vs.* formyl, and hydrogen *vs.* acetyl shift.

Scheme 2



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a X=H, Y=H
b X=H, Y=CH_3
c X=CH_3, Y=H
d X=CH_3, Y=CH_3

The energy profiles of the supposed [1,2]-shifts were constructed by force gradient geometry optimization [7] of all internal molecular coordinates except the reaction coordinate, which was fixed at certain values. The valence angle C(2)–C(3)–H was chosen as the reaction coordinate for the [1,2]-hydrogen shift, the C(2)–C(3)–C(y) angle for the [1,2]-alkyl shift and the C(1)–C(2)–C(3) angle for the [1,2]-acyl shift. In other words, minimum energy reaction paths were calculated for hydrogen, alkyl and acyl migrations in the chosen model substrates. The transition state of each studied [1,2]-shift was located as the energy maximum with respect to the corresponding reaction coordinate. For this purpose several optimizations at small intervals, usually of 2° near each energy maximum, were performed. These calculations were done with the aid of the MONSTERGAUSS 80 program [8] using a double-zeta (DZ) (*4s2p/2s*) [9] basis set. Single point calculations at the DZ-energy maxima were performed using larger double-zeta plus polarization (DZ+P) basis sets [9], namely (*4s2p1d/2s1p*) for C_3H_2O and (*4s2p1d/2s*) for C_4H_4O species (denoted DZ+P//DZ). Electron correlation energy corrections from singly and doubly excited states at these points were calculated using the self-consistent electron pairs (SCEP) method [10] at the DZ-level. The values obtained in this way are denoted DZ+SCEP//DZ. The DZ+SCEP//DZ calculations were performed using a local *IBM* version of GAUSSIAN 76 [11], to which the modified SCEP program was appended as a separate link [12]. In these calculations for the C_3H_2O-species, the four *1s* core orbitals were kept frozen to substitution. For the C_4H_4O-species, however, the twelve lowest MO's were left uncorrelated so as to keep the CPU-time consumption reasonable. In order to have available compatible results for the three models studied, *Hartree-Fock* (*HF*) calculations were performed for the C_3H_2O-species also with the (*4s2p1d/2s*) basis set.

Only singlet ground states were considered since it has been demonstrated previously [5] [6] that the ground state of unsubstituted vinylidene is a singlet and since the calculated lowest triplet unrestricted *HF*-energy (for a singlet transition-state geometry, see *Table 1*) is about 60 kcal/mol higher than the lowest singlet *HF*-energy. The difference E(DZ+P//DZ)−E(DZ) is considered to be the polarization correction, since polarization and correlation energies are approximately additive (*cf.* [6]). The difference between two calculated values of E(DZ+SCEP//DZ) plus polarization correction is taken to be the energy difference (ΔE) between the corresponding species.

3. Results and discussion. – Calculated energies of the studied C_3H_2O- and C_4H_4O-species are listed in *Table 1.* The calculated structural parameters, fully optimized at the DZ-level, are given in *Table 2.* Perspective drawings of the transition state species are shown in *Figures a–f.*

The two cases of [1,2]-shifts defined in the *Introduction* can be clearly distinguished in terms of orbital symmetry. In the case of [1,2]-acyl shifts (**2a**, **2b** and **2c**), molecular conjugation is disrupted, and therefore one cannot expect orbital symmetry constraints on the transition state. Calculations along the chosen minimum energy reaction path for this case give a unique transition state structure²) (in short: transition state) **2**. In the case of [1,2]-hydrogen or methyl shift, one can expect two symmetry constrained planar structures of extremal energy: **3**, with *anti*-configuration of the substituents X and Y, and **4**, with *syn*-configuration of X and Y. A preliminary 6-31G [13] unconstrained geometry optimization for the [1,2]-hydrogen shift in propynal (**1a**), starting from a twisted structure (carbonyl and ring planes orthogonal) leads to the structure **3** being slightly favored (by *ca.* 2 kcal/mol) with respect to **4** *(Table 1).* In the following calculations, therefore, only structure **3** was considered as the transition state for the [1,2]-hydrogen or alkyl shift.

The described reaction path procedure for the location of saddle points on a reaction energy surface is only a crude approximation. However, the reaction studied here has a precedent, the methyl isocyanide → methyl cyanide rearrangement [14], for which a rigorous location of the transition state, involving cal-

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²) In this paper we use the word 'structure' in the sense of 'instantaneous structure' or 'fixed spatial arrangement of a given set of atoms', not necessarily corresponding to a molecule, which some authors call 'nuclear arrangement', 'atom configuration' or 'geometry'.

Table 1. *Calculated energies (E* in atomic units*) of C_3H_2O and C_4H_4O species along the α-alkynone → acyl-vinylidene* (**1** → **5**) *rearrangement paths and energy differences (ΔE* in kcal/mol*)*

Structure	E(6-31G)	E(DZ)[a])	E(DZ + P//DZ)[b]) pol. corr.[c])	E(DZ + SCEP//DZ)[d]) E(DZ + SCEP//DZ) + pol. corr.	ΔE
Propynal (**1a**)	– 189.4591	– 189.4925	– 189.5833	– 189.8320	
			– 0.0908	– 189.9228	0.0
			– 189.5744[e])		
H/H-*anti*-transition	– 189.3631	– 189.3977	– 189.5102	– 189.7135	
state **3a**			– 0.1125	– 189.8260	60.7
			– 189.4853[e])		
H/H-*syn*-	– 189.3599				
structure **4a**					
Formyl-transition	– 189.3444	– 189.3780	– 189.4922	– 189.7281	
state **2a**			– 0.1142	– 189.8423	50.5
			– 189.4872[e])		
Formyl-vinylidene (**5a**)	– 189.4000	– 189.4344	– 189.5299	– 189.7652	
			– 0.0955	– 189.8674	34.8
			– 189.5255[e])		
2-Butynal (**1b**)		– 228.5310	– 228.6339	– 228.7090	
			0.1029	– 228.8119	0.0
H/CH$_3$-*anti*-transition		– 228.4180	– 228.5347	– 228.5992	
state **3b**			– 0.1167	– 228.7159	60.2
Formyl-transition		– 228.4177	– 228.5423	– 228.5933	
state **2b**			– 0.1246	– 228.7179	60.0
Formyl-methyl-		– 228.4631	– 228.5712	– 228.6115	
vinylidene (**5b**)			– 0.1081	– 228.7196	57.9
Butynone (**1c**)		– 228.5307	– 228.6335	– 228.7129	
			– 0.1028	– 228.8157	0.0
CH$_3$/H-*anti*-transition		– 228.4380	– 228.5597	– 228.6065	
state **3c**			– 0.1217	– 228.7282	54.9
Acetyl-transition state **2c**		– 228.4186	– 228.5419	– 228.6001	
			– 0.1233	– 228.7234	57.9
Acetyl-transition state **2c**,		– 228.3132			
triplet					
Acetyl-vinylidene (**5c**)		– 228.4725	– 228.5784	– 228.6300	
			– 0.1059	– 228.7359	50.0

[a]) E(DZ) = energy calculated using double-zeta basis sets. [b]) E(DZ + P//DZ) = E(DZ) plus polarization calculated at the DZ-level. [c]) Pol. corr. = E(DZ + P//DZ) – E(DZ). [d]) E(DZ + SCEP//DZ) = E(DZ) plus electron correlation calculated with SCEP at the DZ-level. [e]) *HF*-energies for C_3H_2O with the (*4s2p1d/2s*) basis set.

culation of its vibrational modes, has yielded a structure very similar to the ones described below. These results indicate that the reaction path in the vicinity of the transition state for this type of reaction is dominated by a single internal degree of freedom, which we describe here approximately as the bending of the C–C–H or C–C–C valence angle[3]).

The transition states **3a** and **3c** for the [1,2]-hydrogen shift of **1a** and **1c** are bridged-hydrogen structures. The C(3)–H distances 1.248 and 1.247 Å are

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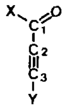
[3]) We thank a referee for stressing to us the importance of this justification of our approach. A general discussion of the problem for any transition state can be found in recent theoretical work (*cf.* [15]).

almost the same as the one calculated for the rearrangement of the unsubstituted vinylidene to acetylene (1.260 Å) [6], and the C(2)–C(3)–H angle (reaction coordinate) is 68° *(Table 2)*. The transition state **3b** for the [1,2]-methyl shift has a C(3)–C(y) distance of 1.806 Å and the C(2)–C(3)–C(y) angle (reaction coordinate) is 77°. The above C–C distance is comparable to the value found for the DZ-transition state (1.815 Å) of the $CH_3NC \rightleftarrows CH_3CN$ isomerization, but longer than that found for the DZ+P transition state (1.740 Å) of that same reaction [14] [16].

The transition states **2** for the [1,2]-acyl shift are carbon-bridged structures, with the plane of the acyl group almost perpendicular to the plane of the three ring C-atoms. The C(1)–C(2) distance here is 1.83–1.85 Å, a value shorter than the one calculated for the C(1)–C(2) distance in the transition state of the decarbonylation of propadienone (1.922 Å with 4-31G, 1.937 Å with 6-31G**) [17],

Table 2. *Calculated geometric parameters for C_3H_2O- and C_4H_4O-species by force-gradient geometry optimization* (bond lengths *r* in Å, bond angles *a* and dihedral angles θ in °)

Structure		**1a**	**1b**	**1c**
		X=H	X=H	X=CH_3
		Y=H	Y=CH_3	Y=H
	r[C(1)–O]	1.21875	1.22083	1.22248
	r[C(1)–X]	1.08267	1.08355	1.50690
	r(C(1)–C(2)]	1.44821	1.44349	1.45776
	r[C(2)–C(3)]	1.19854	1.19972	1.19838
	*r*[C(3)–Y]	1.05600	1.46673	1.05565
	a[O–C(1)–C(2)]	123.998	124.361	121.177
	a[X–C(1)–O]	120.738	120.247	122.504
	r[C(y)–H]		1.0824–1.0831	
1	*r*[C(x)–H]			1.0800–1.0844
	a[C(3)–C(y)–H]		110.4–110.7	
	a[C(1)–C(x)–H]			109.7–110.1

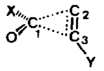
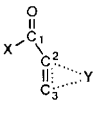
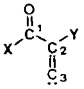
Structure		**2a**	**2b**	**2c**
		X=H	X=H	X=CH_3
		Y=H	Y=CH_3	Y=H
	r[C(1)–O]	1.19972	1.20375	1.20048
	r[C(1)–C(2)]	1.83344	1.84972	1.84940
	r[C(2)–C(3)]	1.25904	1.26205	1.25784
	r[C(3)–Y]	1.06143	1.47583	1.06141
	r[C(1)–X]	1.07656	1.07754	1.49865
	a[O–C(1)–C(2)]	125.744	127.894	120.755
	θ[O–C(1)–C(2)–C(3)]	87.054	83.114	88.925
	a[C(1)–C(2)–C(3)]	70	68	72
	a[C(2)–C(3)–Y]	190.538	192.572	189.214
2	*a*[X–C(1)–C(2)]	105.518	104.292	109.866
	a[X–C(1)–C(2)–C(3)]	247.435	242.887	252.166
	r[C(y)–H]		1.0822–1.0830	
	r[C(x)–H]			1.0799–1.0832
	a[C(3)–C(y)–H]		108.3–110.6	
	a[C(1)–C(x)–H]			109.2–110.0

Table 2 (continued)

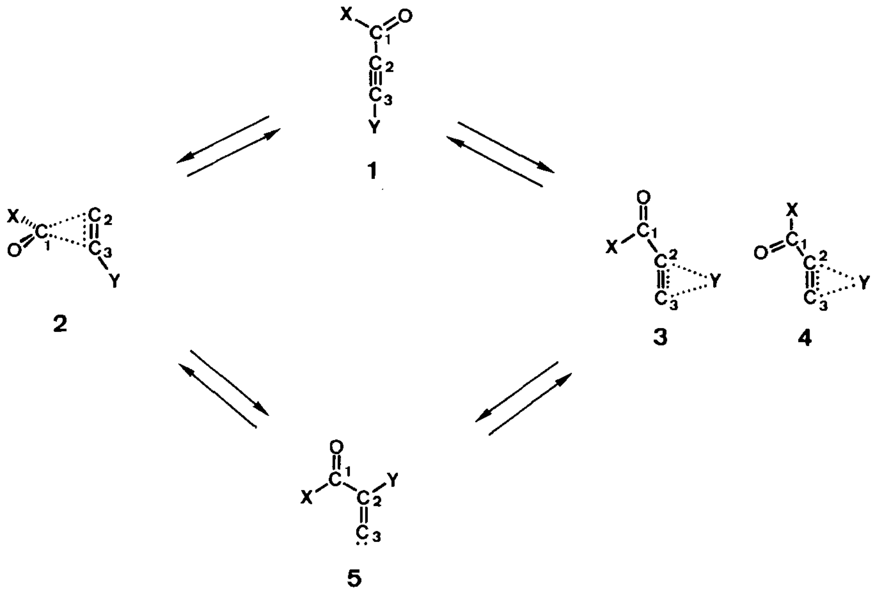
Structure		**3a** X=H Y=H	**3b** X=H $Y=CH_3$	**3c** $X=CH_3$ Y=H
 **3**	*r*[C(1)–O]	1.21841	1.22365	1.22249
	r[C(1)–C(2)]	1.44509	1.43452	1.45513
	r[C(2)–C(3)]	1.26214	1.26528	1.26138
	r[C(3)–Y]	1.24812	1.80644	1.24667
	r[C(1)–X]	1.08233	1.08299	1.50551
	a[O–C(1)–C(2)]	124.332	124.733	121.268
	a[C(1)–C(2)–C(3)]	185.344	188.121	184.574
	a[C(2)–C(3)–Y]	68	77	68
	a[C(2)–C(1)–X]	113.642	113.719	115.079
	r[C(y)–H]		1.0753–1.0822	
	r[C(x)–H]			1.0798–1.0835
	a[C(3)–C(y)–H]		99.8–123.2	
	a[C(1)–C(x)–H]			109.1–110.3

Structure		**5a** X=H Y=H	**5b** X=H $Y=CH_3$	**5c** $X=CH_3$ Y=H
 **5**	*r*[C(1)–O]	1.21860	1.22000	1.22013
	r[C(1)–C(2)]	1.47820	1.48716	1.51808
	r[C(2)–C(3)]	1.31450	1.31613	1.31066
	r[C(1)–X]	1.08230	1.08246	1.54269
	r[C(2)–Y]	1.08010	1.52388	1.08339
	a[O–C(1)–C(2)]	122.336	122.321	121.243
	a[C(1)–C(2)–C(3)]	125.914	117.552	125.436
	a[O–C(1)–X]	120.670	120.393	122.653
	a[C(1)–C(2)–Y]	117.523	119.471	117.220
	r[C(y)–H]		1.0805–1.0819	
	r[C(x)–H]			1.0850–1.0868
	a[C(2)–C(y)–H]		110.4–111.4	
	a[C(2)–C(x)–H]			109.8–110.1

and the C(1)–C(2)–C(3) angle (reaction coordinate) is 68–72°. It is important to note that the bond lengths within the migrating methyl, formyl and acetyl groups in the transition state do not differ significantly from those in the corresponding *α*-alkynones **1** or acyl-vinylidenes **5**. The initial triple bond C(2)–C(3) of the studied *α*-alkynones **1** is stretched in the transition states **2** and **3** to about 1.26 Å, a value close to the C=C bond length in acyl-vinylidenes **5** (1.31 Å). The initially linear acetylenic substructure C(2)–C(3)–Y in **1** is only slightly bent (189 to 192°) in the transition state **2**. Thus both calculated transition states **2** and **3** are more similar to weak molecular complexes than to stable ring molecules.

The calculated activation energy for the [1,2]-formyl shift rises from 50.5 kcal/mol in propynal (**1a**) to 60.0 kcal/mol in 2-butynal (**1b**) *(Table 1)*. For propynal (**1a**) the [1,2]-formyl shift has a lower activation energy (50.5 kcal/mol) than the [1,2]-hydrogen shift (60.7 kcal/mol); this is due to the much larger electron correlation

Scheme 3



in the transition state **2a** than in **3a**. In the case of 2-butynal (**1b**), the correlation correction to the energy of the formyl transition state **2b** is about half of that for **2a** and about the same as that for **3b**. We conclude that the [1,2]-acyl shift in α-alkynones (**1**) with Y = alkyl is less favorable than that with Y = H.

The [1,2]-acetyl shift in butynone (**1c**) requires about 20% more activation energy (57.9 kcal/mol) than the [1,2]-formyl shift (50.5 kcal/mol) in propynal (**1a**). On the other hand, the [1,2]-hydrogen shift in butynone (**1c**) is more favorable (54.9 kcal/mol) than the [1,2]-acetyl shift in the same compound (57.9 kcal/mol) and requires less activation energy even than the [1,2]-hydrogen shift (60.7 kcal/mol) in propynal (**1a**).

The calculation for the C_3H_2O-species with the (*4s2p/2s*) basis set predicts, as expected, a somewhat less favored [1,2]-hydrogen shift, when compared to the calculations with both the (*4s2p/2s*) and the (*4s2p1d/2s1p*) basis sets. These differences, however, do not affect the trend of the substituent effects. Furthermore, no qualitative change in that trend is to be expected due to electron correlation, since calculated electron correlation effects in the transition state of C_4H_4O are almost equal for the [1,2]-shifts of hydrogen, methyl, formyl or acetyl. We are, therefore, permitted to consider these effects to hold also for larger molecules.

In order to predict whether alkyl or acyl substituents are more prone to [1,2]-shift in an α-alkynone cyclization, we have to extrapolate the present results to C_5 and larger species. Since methyl substitution at the acetylenic C-atom enhances the activation energy for the [1,2]-acyl shift by *ca.* 8 kcal/mol, and since the [1,2]-methyl shift in 2-butynal (**1b**) has an activation energy of 60.2 kcal/mol, one could expect a value of about 66 kcal/mol for the [1,2]-acetyl shift and of 60 kcal/mol or

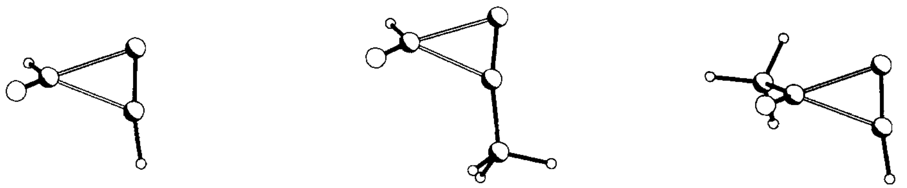


Fig. a. Propynal, formyl-transition state **2a**

Fig. c. 2-Butynal, formyl-transition state **2b**

Fig. e. Butynone, acetyl-transition state **2c**

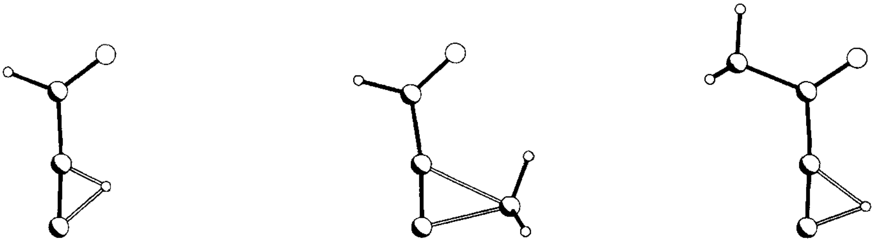


Fig. b. Propynal, hydrogen-transition state **3a**

Fig. d. 2-Butynal, methyl-transition state **3b**

Fig. f. Butynone, hydrogen-transition state **3c**

Figure. *Perspective drawings of the calculated transition states* **2a**–**c** *and* **3a**–**c** (small empty spheres = H-atoms; large empty spheres = O-atoms; large shaded spheres = C-atoms)

less for the [1,2]-methyl shift in 3-pentyne-2-one (**1d**). In support of this extrapolation we note that the calculated activation parameters for the rearrangements of HCN to HNC [18] and of CH_3NC to CH_3CN [14] are approximately the same as the ones obtained in this work. We conclude, therefore, that a H-atom or an alkyl group will compete favorably with an acyl group in the [1,2]-shift of an acetylenic substituent in α-alkynones **1** to the corresponding acyl-vinylidene **5**.

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