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Dimerization of Two Alkyne Units: Model Studies, Intermediate Trapping Experiments, and Kinetic Studies

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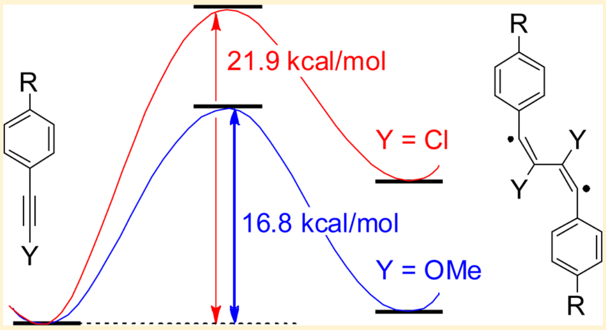
Supporting Information

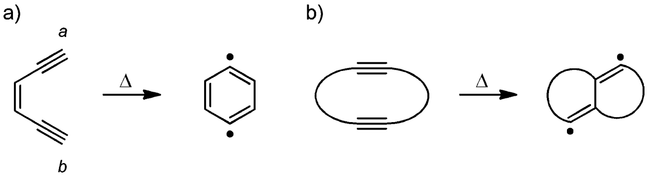
ABSTRACT: By means of high level quantum chemical calculations (B2PLYPD and CCSD(T)), the dimerization of alkynes substituted with different groups such as F, Cl, OH, SH, NH_2, and CN to the corresponding diradicals and dicarbenes was investigated. We found that in case of monosubstituted alkynes the formation of a bond at the nonsubstituted carbon centers is favored in general. Furthermore, substituents attached to the reacting centers reduce the activation energies and the reaction energies with increasing electronegativity of the substituent ($F > OH > NH_2$, $Cl > SH$, H, CN). This effect was explained by a stabilizing hyperconjugative interaction between the σ^* orbitals of the carbon-substituent bond and the occupied antibonding linear combination of the radical centers. The formation of dicarbenes is only found if strong π donors like NH_2 and OH as substituents are attached to the carbene centers. The extension of the model calculations to substituted phenylacetylenes (Ph−C≡C−Y) predicts a similar reactivity of the phenylacetylenes: $F > OCH_3 > Cl > H$. Trapping experiments of the proposed cyclobutadiene intermediates using maleic anhydride as dienophile as well as kinetic studies confirm the calculations. In the case of phenylmethoxyacetylene (Ph−C≡C−OCH_3) the good yield of the corresponding cycloaddition product makes this cyclization reaction attractive for a synthetic route to cyclohexadiene derivatives from alkynes.



INTRODUCTION

The thermal cyclization of (Z)-hex-3-ene-1,5-diyne to 1,4-dehydrobenzene at temperatures over 200 °C was studied in the 1970s by R. G. Bergman et al.[1−3] (Scheme 1a). During the last decades, the Bergman cyclization was investigated by various authors and became a very attractive method to generate highly reactive diradical intermediates en route to new aromatic rings. One aim was to reduce the required activation energy to achieve a cyclization reaction at ambient temperature.[4−6] Studies revealed that the distance (a−b in Scheme 1a) between the terminal carbon atoms of the triple bonds strongly affects the activation energy for ring closure. If this distance is less than 3.2 Å by connecting ends of the triple bonds through a larger cycle, the cyclization proceeds rapidly at ambient temperature.[7,8]

Scheme 1. (a) Bergman Cyclization, (b) Formation of a 1,3-Butadiene-1,4-diyl Unit by Transannular Ring Closure between Two Parallel Oriented Alkyne Units



Two parallel oriented alkyne units in close proximity, which are not connected by a double bond, tend to react with each other by forming a 1,3-butadiene-1,4-diyl unit as intermediate, which is shown in Scheme 1b. An example for a molecule with such a behavior is tetradehydrodinaphtho[10]annulene (**1**), which reacts via the diradical **2** to zethrene (**3**) (Scheme 2).[9] 1,6-Didehydro[10]annulene (**4**) (Scheme 3), which is only stable below −90 °C, reacts at higher temperatures via the 1,5-didehydronaphthalene (**5**) to naphthalene (**6**).[10]

In the two examples shown in Schemes 2 and 3, the distances between the central π units are rather short (2.81 Å for **1** and 2.93 Å for **4** calculated using B3LYP/6-311++G**), which lowers the activation energy for a transannular bond formation considerably. When the two alkyne units are fixed at a distance of 3.0 Å (3.04 Å calculated using B3LYP/6-311++G**) as in 1,6-cyclodecadiyne (**7**)[11] the transannular reaction occurs only at higher temperatures (Scheme 4). For **7**, an activation energy of 28.9 kcal/mol was reported.[12] During our studies of **7**, **8**, and related heterocyclic derivatives,[11,13] we noticed a lower activation energy when X in **7** was replaced by hetero atoms.[14] This observation encouraged us to look closer at the

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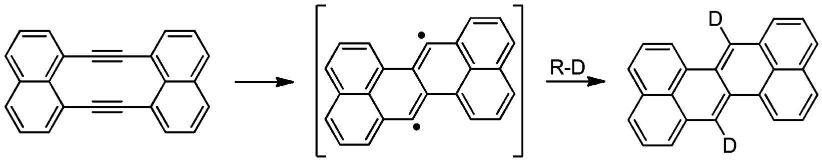
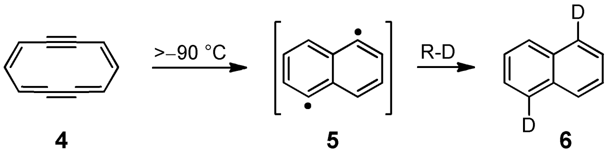
Scheme 2. Generation of Zethrene (3) from Tetradehydrodinaphtho[10]annulene (1)



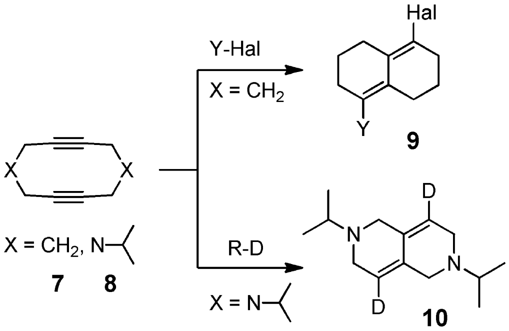
1 2 3

Scheme 3. Thermal Rearrangement of 1,6-Didehydro[10]annulene (4) to 1,5-Didehydronaphthalene (5)



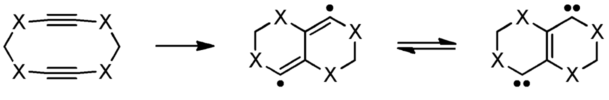
4 5 6

Scheme 4. Reactions of 7 with Halogens or Pseudohalides to 9 and of 8 with Hydrocarbons to 10



7 8 9 10

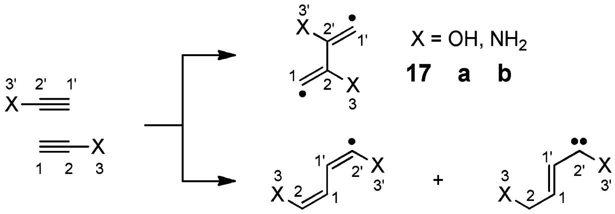
Scheme 5. Cyclic Model Systems to Test the Influence of Hetero Atoms on the Activation Energy



X = O, NH

11 a b 12 13

Scheme 6. Possible Dimerization Products from Two Alkynes 14a and 14b



X = OH, NH$_2$

17 a b

X = OH, NH$_2$

14·14 a b 15 16

role of heteroatoms in 10-membered rings such as **7** or **8** and in simple alkynes such as **14** (Schemes 5 and 6).[15] Model calculations on **11a** and **11b** revealed that oxygen centers or NH groups next to the triple bonds (Scheme 5) reduce the activation energy of the ring closure considerably. It furthermore shows that the resulting 1,4-diradicals (**12a,b**) are energetically similar to the corresponding 1,4-dicarbenes **13a,b** in Scheme 5. Because of the unexpected behavior of **11a,b**, we calculated the C−C bond formation of two alkyne units substituted by one or two donor groups (see Scheme 6). We found that the C1−C1′ bond formation is favored over the C2−C2′ bond closure. Again donor groups lower the C−C bond formation to 1,4-diradicals (**15**, **17**) and even 2-butene-1,4-dicarbene (**16**).

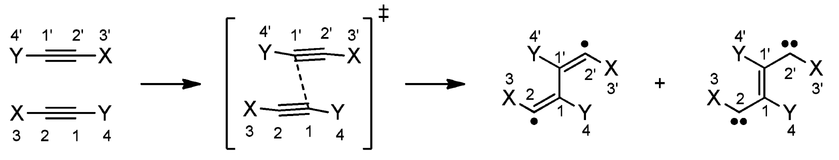
In this paper, we present the results of model calculations on alkynes with different substituents such as F, Cl, OH, SH, NH$_2$, and CN. Moreover, the dimerization of substituted phenylacetylenes was calculated by using B2PLYPD/6-31G*. Experimental investigations concerning the dimerization of substituted phenylacetylenes in the presence of maleic anhydride confirm the calculations with regard to the substituent-dependent reactivity of the alkynes.

■ RESULTS AND DISCUSSION

Model Studies on Substituent Effects in the Dimerization of Alkynes. To determine the dependency of the dimerization energy on substituents, the dimerization of the alkynes **18** (see Scheme 7), which feature the substituents X and Y, was analyzed via *ab initio* methods. For consistent numerations and designations of starting materials, transition states and products of the dimerization were regarded in such a way that, after the reaction, substituent X comes to stay directly beside the radical or carbene center, while substituent Y is bound to the C atoms that form the new bond. Thus, both dimerization pathways can be described via one numbering system due to the use of arabic and roman numbers per molecule (H−C≡C−CN with X = H, Y = CN (**18a-VII**) and with X = CN, Y = H (**18g-I**)). Furthermore, it was assumed that the spin multiplicity remains constant during the reaction. Thus, the calculated diradicals and dicarbenes exhibit singlet states. The stationary points of this formal 1,1′ dimerization were optimized using the double hybrid method B2PLYPD by Grimme.[16] As basis set, aug-cc-pVDZ[17] has been used. The energies of the stationary points were calculated using CCSD(T).[18] Here, the 6-311++G(3d,2p)[19] basis set was employed. This combination of methods was chosen because for thermal cyclization of **7** (Scheme 4), we have obtained values[15] with this combination showing a very high consistency to experimental data.[4,6] Furthermore, single point calculations were performed on the B2PLYPD-optimized structures by means of (12/10)CASSCF and (12/10)CASPT2. The cc-pVTZ[17] basis was employed. For the 1,1′ dimerization of **18** calculated data are shown in Tables 1 and 2, Tables S1 and S2 of Supporting Information, Figures 1 and 2, and Figure S1 of Supporting Information.

As shown for the dimerization of **14** and cyclization of **11**, the energy values of the B2PLYPD method are in good accordance with those of the CCSD(T) approximation.[15] The energies obtained from (12,10)CASSCF calculations are as

Scheme 7. Dimerization of Substituted Alkynes 18·18 to Diradicals 20 and Dicarbenes 21



18·18 **19** **20** **21**

X = H, F, Cl, OH, SH, NH_2, CN
a b c d e f g

Y = H, F, Cl, OH, SH, NH_2, CN
I II III IV V VI VII

Table 1. Energies (Δ*E* in kcal/mol) of the Transition States (19) and Products (20 and 21) Relative to the Corresponding Starting Materials (18·18) Calculated by Means of B2PLYPD/aug-cc-pVDZ[a]

			19		20		21	
	X	Y	*R* [Å]	Δ*E*	*R* [Å]	Δ*E*	*R* [Å]	Δ*E*
a-I	H	H	1.689	31.75	1.531	30.17		
a-II	H	F	1.955	13.83	1.473	−0.28		
a-III	H	Cl	1.893	26.84	1.485	17.08		
a-IV	H	OH	1.923	18.73	1.496	8.59		
a-V	H	SH	1.804	28.74	1.531	25.63		
a-VI	H	NH_2	1.797	23.71	1.535	20.98		
a-VII	H	CN	1.741	35.51	1.539	33.94		
b-I	F	H	2.000	17.94	1.458	−2.55		
c-I	Cl	H	1.950	18.22	1.474	4.38		
d-I	OH	H	1.968	18.04	1.469	3.96	1.382	4.12
d-II	OH	F	2.130	3.79	1.448	−25.56	1.372	−27.78
d-III	OH	Cl	1.993	16.62	1.466	−1.97	1.365	−10.42
d-IV	OH	OH	2.054	11.11	1.461	−11.62	1.389	−22.12
d-VI	OH	NH_2	1.965	14.07	1.501	1.81	1.418	−13.93
d-VII	OH	CN	1.896	21.87	1.504	12.37	1.396	18.14
e-I	SH	H	1.937	17.30	1.490	7.79		
e-II	SH	F	2.124	4.91	1.462	−19.19		
e-V	SH	SH	1.893	20.81	1.536	14.58		
f-I	NH_2	H	1.954	19.04	1.482	7.00	1.367	−4.02
f-II	NH_2	F	2.166	2.30	1.458	−24.31	1.369	−45.55
f-IV	NH_2	OH	2.049	11.66	1.477	−8.61	1.377	−40.97
f-VII	NH_2	CN	1.869	17.72	1.543	17.53	1.391	4.76
g-I	CN	H	1.857	20.46	1.492	14.04		
g-II	CN	F	2.042	9.62	1.454	−12.02		
g-IV	CN	OH	1.991	13.26	1.482	−1.76		
g-VII	CN	CN	1.834	27.71	1.506	22.61		

[a] The distances *R* of C1−C1′ are also given.

expected too high because no dynamic correlation is taken into account in this method (Table S1, Supporting Information). The occupation numbers of the frontier orbitals (n_1 and n_2), which were taken from the (12,10)CASSCF wave function, show that the dicarbenes possess the closed shell singlet state whereas the diradicals are open shell species (Table S2, Supporting Information). The (12,10)CASPT2 energies for the diradicals are lower whereas the (12,10)CASPT2 energies for the dicarbenes are higher than those calculated using B2PLYPD and CCSD(T) (Table S3, Supporting Information). This is because the CASPT2 method overestimates the electron correlation of unpaired electrons relative to paired electrons.[14b,15,20]

If the monosubstituted alkynes (X = H, Y ≠ H, and X ≠ H, Y = H) are looked at, it can be seen that the 1,1′ dimerization of the alkynes with X ≠ H, Y = H (**18-I**; Figure 1) usually turns out to be better than the 1,1′ dimerization of the corresponding alkynes with X = H, Y ≠ H (**18a**). The alkynes are identical, so this means that the formation of a bond at the nonsubstituted carbon centers is in general favored for monosubstituted alkynes. One exception of this rule is the fluoro-substituted alkyne **18a-II**.

Having a look at the C1−C1′ dimerizations within the groups **18a**, **18d**, **18e**, **18f**, and **18g** (Figures 1, 2 and Figure S1 of Supporting Information), it becomes evident that the stability of the diradical products **20** increases with higher electronegativity of the atom bound to C1 (F > OH > NH_2, Cl > SH, H, CN). While diradical **20a-I** (X = H, Y = H, Figure 1 and Table 3) exhibits an energy of about 29 kcal/mol with regard to the monomers, the destabilization of diradical **20a-III** (X = H, Y = Cl) amounts to 16 kcal/mol relating to the alkynes **18a-III·18a-III**. In case of the fluoro alkynes **18a-II·18a-II**,

Table 2. Energies (ΔE in kcal/mol) of the Transition States (19) and Products (20 and 21) Relative to the Corresponding Starting Materials (18·18) Calculated by Means of CCSD(T)/6-311++G(3d,2p)//B2PLYPD/aug-cc-pVDZ

			ΔE		
	X	Y	19	20	21
a-I	H	H	33.43	28.59	
a-II	H	F	16.98	−1.72	
a-III	H	Cl	28.53	15.81	
a-IV	H	OH	21.06	7.98	
a-V	H	SH	30.49	25.57	
a-VI	H	NH_2	26.40	20.90	
a-VII	H	CN	33.46	28.24	
b-I	F	H	21.12	−2.94	
c-I	Cl	H	22.47	7.95	
d-I	OH	H	21.47	5.53	7.99
d-II	OH	F	7.51	−22.73	−24.44
d-III	OH	Cl	19.22	−0.48	−7.69
d-IV	OH	OH	13.75	−9.29	−19.27
d-VI	OH	NH_2	16.91	1.09	−9.64
d-VII	OH	CN	22.07	9.14	16.24
e-I	SH	H	21.39	11.84	
e-II	SH	F	8.50	−14.96	
e-V	SH	SH	22.74	16.53	
f-I	NH_2	H	23.43	11.47	−0.08
f-II	NH_2	F	7.06	−17.98	−39.80
f-IV	NH_2	OH	15.59	−3.71	−37.62
f-VII	NH_2	CN	19.97	15.81	3.47
g-I	CN	H	26.26	18.80	
g-II	CN	F	14.39	−5.78	
g-IV	CN	OH	17.13	3.27	
g-VII	CN	CN	30.30	24.04	

diradical **20a-II** (X = H, Y = F) is even more stable by 2 kcal/mol than the starting materials. The activation energies decrease, even though less strongly, with increasing electronegativity of the atom bound to C1. This is in accordance with the experimentally observed higher reactivity of fluoroacetylenes in contrast to chloroacetylenes,[21] which was also confirmed by UB3LYP calculations.[22] This behavior was explained by the fact that fluoroacetylenes have smaller singlet−triplet gaps than chloroacetylenes and thus more easily undergo dimerization.[22] A glance at the calculated singlet−triplet gaps between **18a** and **22a** (Scheme 8a) shows that this argument cannot explain the obtained reactivity series F > OH > NH_2, Cl > SH > H, CN. For example, the singlet−triplet gap for **18a-V** (Y = SH; 3.11 eV) is almost as large as the one for **18a-II** (Y = F; 3.13 eV), whereas the calculated reactivity of **18a-II** is much higher than that of **18a-V** (Figure 1 and Table 2). Furthermore, if one follows the singlet−triplet gap argument, then the amino-substituted alkyne **18a-VI** should be the most reactive compound, which is definitely not the case (Table 2).

The fact that electronegative elements (like fluorine, oxygen, or chlorine) bound to C1 stabilize the formed diradicals and dicarbenes relates to Hoffmann's early finding that the electronegative ligands favor a singlet ground state of carbenes.[23] One explanation for this series (F > OH > Cl, NH_2 > SH, H, CN) within the investigated groups is a hyperconjugative interaction between the occupied antibonding linear combination of the radical centers ($n_{C2/C2'}$) and the two σ^*_{C-Y} orbitals in the diradicals **20a** (Scheme 8b). The higher electronegativity of fluorine compared with hydrogen lowers the σ^* orbitals of **20a-II** compared with the corresponding orbitals in **20a-I**. Accordingly, the stabilizing interactions of the σ^* orbitals with the occupied antibonding linear combination ($n_{C2/C2'}$) are more pronounced for diradicals having electronegative elements (like fluorine, oxygen, or chlorine) bound to C1. This interaction is corroborated by a NBO[24] analysis (Scheme 8c) of the wave functions: For the energy of the $n_{C2/C2'} \rightarrow \sigma^*$ interaction ($E^{(2)}$) following order is found: F > OH > Cl > NH_2 > SH > H > CN.

Regarding the C1−C1′ bond formation of **18d** (X = OH), it can be seen that the OH group even leads to a strong decrease of the activation barrier and the diradical state (Figure 2) if it is bound to the C2 atom. In the case of **18d-II** (Y = F) and **18d-IV** (Y = OH), the activation barrier only amounts to 7.5 and 13.8 kcal/mol, respectively. Apart from the diradicals **20d**, the dicarbenes **21d** are here found for all substituents Y. It is interesting that for the substituents F, OH, NH_2, and Cl, the

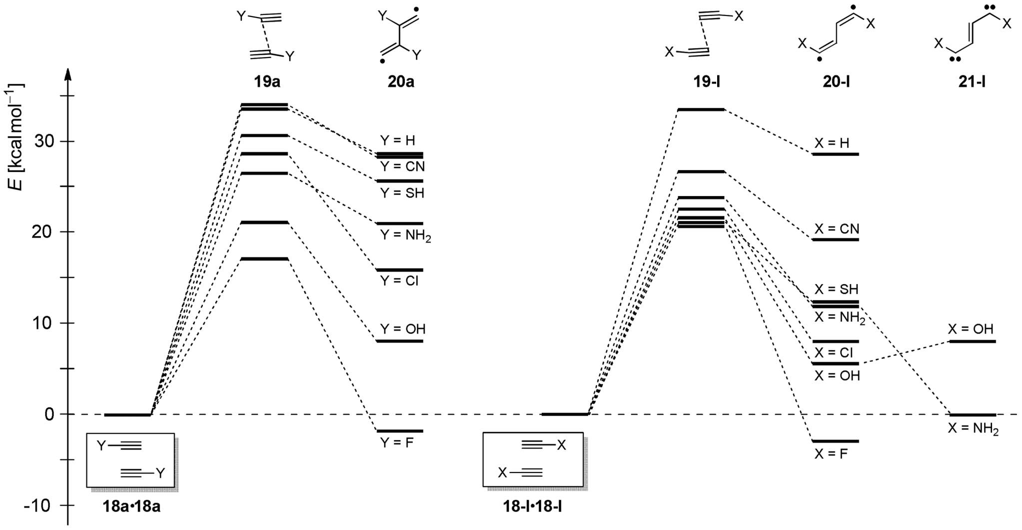


Figure 1. Energy profiles for the C1−C1′ bond formation of **18a·18a** (left) and **18-I·18-I** (right) calculated using CCSD(T)/6-311++G(3d,2p)//B2PLYPD/aug-cc-pVDZ.

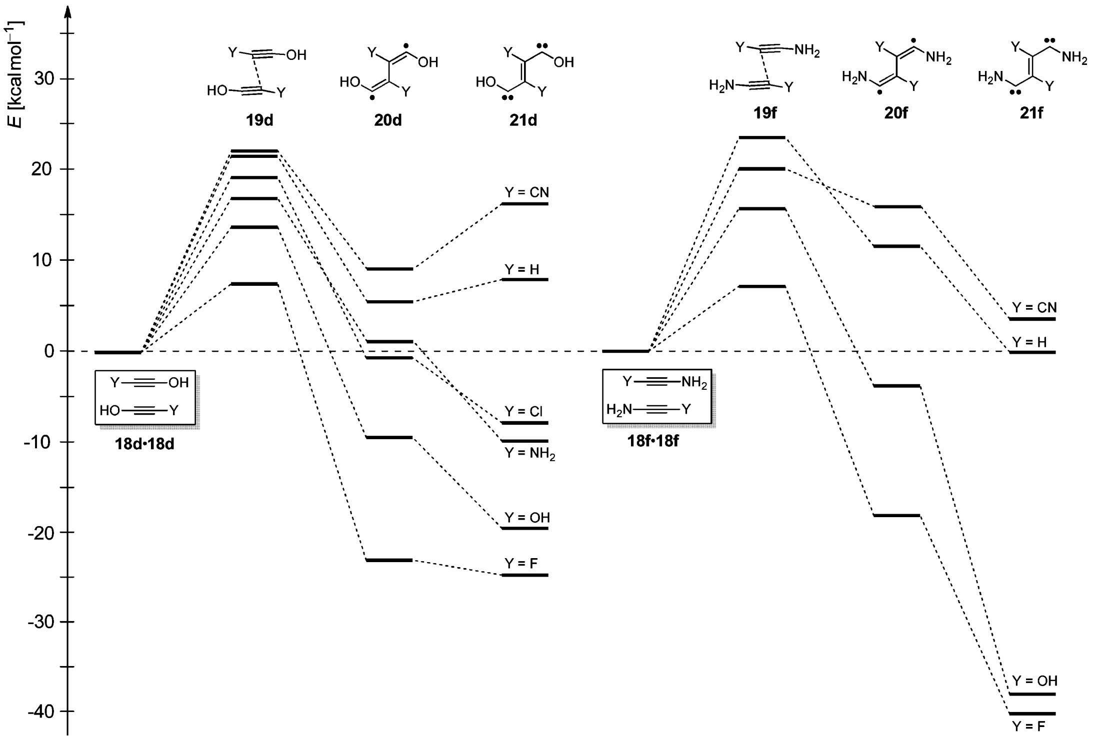


Figure 2. Energy profiles for the C1−C1′ bond formation of **18d·18d** (left) and **18f·18f** (right) calculated using CCSD(T)/6-311++G(3d,2p)//B2PLYPD/aug-cc-pVDZ.

Table 3. Energies (ΔE in kcal/mol) of the Transition States (19a-IV and 19d-I) and Products (20a-IV, 20d-I, and 21d-I) Relative to the Corresponding Starting Materials (18·18)

	X	Y	ΔE^a	ΔE^b	ΔE^c
19a-IV	H	OH	18.73	21.06	22.19
20a-IV	H	OH	8.59	7.98	7.09
19d-I	OH	H	18.04	21.47	20.68
20d-I	OH	H	3.96	5.53	*e*
21d-I	OH	H	4.12	7.99	2.00

[a] B2PLYPD/aug-cc-pVDZ. [b] CCSD(T)/6-311++G(3d,2p)//B2PLYPD/aug-cc-pVDZ. [c] UB3LYP/6-31G*. [e] Optimization using UB3LYP/6-31G* leads to no converged minimum structure.

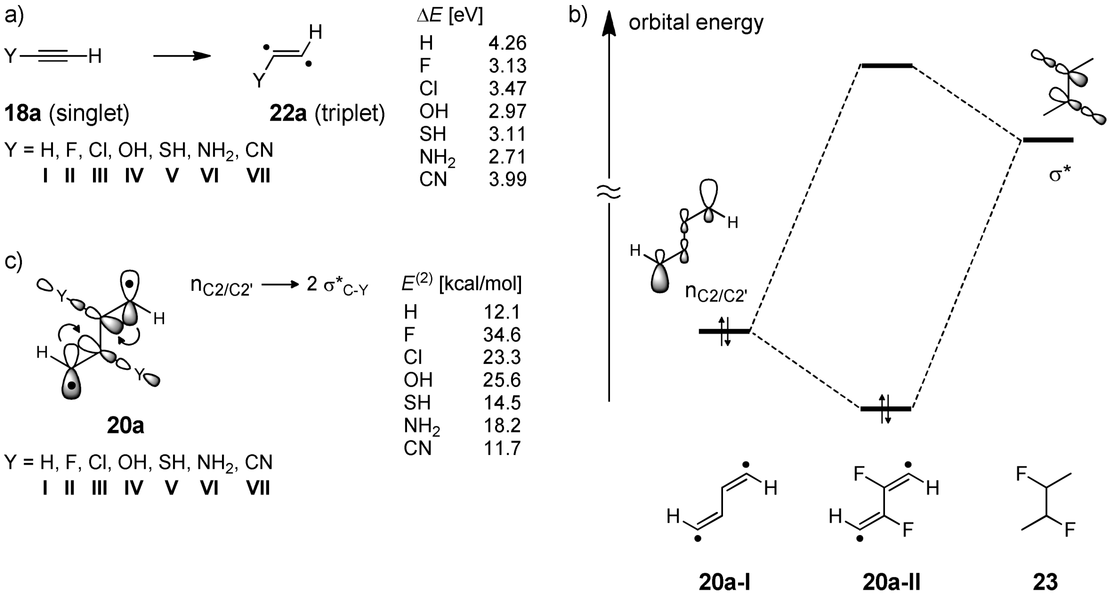
dicarbenes are even more stable than the corresponding diradicals, whereas the diradicals are more stable for the substituents H and CN (Table 2). This is because both H and CN favor a triplet ground state of carbenes, while the dicarbenes **21d** are singlet carbenes.[23b] An amino group bound to C2 (**18f**) exhibits an effect similar to the OH group (**18d**, Figure 2), but the stabilization of the transition states (**19f**) and diradicals (**20f**) is slightly smaller than it is for the OH substituent. The dicarbenes (**21f**) are however more stabilized by the NH group than by the OH group (**21d**), which can be ascribed to the stronger π donor property of the amino group.

A comparison of the dimerization of the alkynes **18d** (X = OH) with the alkynes **18e** (X = SH) reveals different effects caused by the OH and SH group (Figure 2 and Figure S1 of Supporting Information): Like the OH substituent, the SH bound to C2 leads to a decrease of the activation barrier (**19e-I** vs **19a-I**) and more stable diradicals (**20e-I** vs **20a-I**), but if the SH groups are additionally bound to the bond forming C1 atoms, the activation barrier (Figure S1, Supporting Information, **19e-I** vs **19e-V**) and reaction energy (**20e-I** vs **20e-V**) are increased. Contrary to the dicarbenes **21d** (X = OH), no dicarbenes of type **21e** were found for SH at C2. This means that the donor property of SH is not sufficient to enable a configurational change from diradical **20e** to dicarbene **21e**.

A C2-bound CN group (**18g**; Figure S1, Supporting Information) leads to a decrease of the activation barriers (**19g-I** vs **19a-I**) and a stabilization of the diradicals (**20g-I** vs **20a-I**). If an additional CN group is located at C1, the activation and reaction energy of the dimerization of the dinitrile **18g-VII** are higher than those calculated for **18g-I** (Figure S1, Supporting Information).

Dimerization of Substituted Phenylacetylenes. The dimerization of substituted phenylacetylenes (**24**, see Scheme 9) is interesting because these are the simplest representatives of arylacetylenes, which are supposed to be much more reactive than the corresponding alkylacetylenes: While *tert*-butylfluoroacetylene[25] was synthesized at about 120 °C and can be specifically used for thermal cyclotrimerizations,[25] the synthesis of phenylfluoroacetylene was only possible at low temperatures.[26] Higher temperatures lead to thermal polymerization.[27] For phenylchloroacetylenes, a similar behavior was found: While *tert*-butylchloroacetylene is supposed to be thermally stable,[28] Ballester et al. were able to demonstrate that perchlorophenylchloroacetylene was cyclotrimerized at 110−120 °C.[29] UB3LYP[30] calculations confirmed these experimental findings and showed that a dimerization, in which the phenyl groups are bound to the diradical centers, was preferred.[22] The method UB3LYP/6-31G* was used because it is not time-consuming and already delivered good results for other diradicals.[31] In contrast to the phenylhalogenacetylenes (Ph−C≡C−X), the thermal behavior of phenylmethoxyacetylene has not been analyzed yet even though phenylmethoxyacetylene (Ph−C≡C−OMe) can be synthesized in a few steps.[32]

Scheme 8. (a) Singlet-Triplet Gap of 18a Calculated Using B2PLYPD/aug-cc-pVDZ, (b) Hyperconjugative Stabilization of the Occupied Antibonding Linear Combination of the Radical Centers ($n_{C2/C2'}$) in the Fluoro-Substituted Compound 20a-II Compared with 20a-I, and (c) NBO Analysis (B2PLYPD/aug-cc-pVDZ) of the Hyperconjugative Interaction between the Occupied Antibonding Linear Combination of the Radical Centers ($n_{C2/C2'}$) and the Two σ^*_{C-Y} Orbitals in the Diradicals 20a



Scheme 9. Dimerization of Substituted Alkynes 24·24 to Diradicals 26d and 29 and to Dicarbene 27d

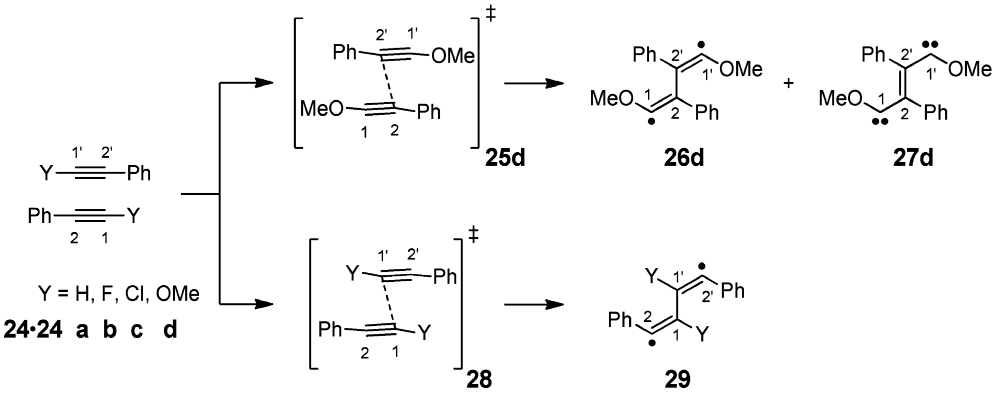


Table 4. Energies (**Δ***E* in kcal/mol) of the Transition States (25d, 28) and Products (26d, 27d, and 29) Relative to the Corresponding Starting Materials (24·24)[a]

	Y	R [Å][b]	ΔE[b]	ΔE[c]	ΔE[d]	ΔE[e]	ΔE[f]	ΔE[g]
28a	H	1.862	18.84	21.81	28.41	49.82	19.82	*h*
29a	H	1.538	15.28	19.17	28.30	33.90	14.39	*h*
28b	F	2.082	6.05	7.48	11.96	33.31	6.41	8.54
29b	F	1.479	−13.62	−11.51	−0.80	−13.34	−17.80	−15.77
28c	Cl	1.988	17.13	17.48	24.82	44.82	16.72	21.88
29c	Cl	1.500	5.21	6.34	21.20	11.48	1.03	0.95
28d	OMe	2.025	10.57	11.72	15.48	42.32	8.48	15.94
29d	OMe	1.508	−2.75	0.25	9.21	24.36	−9.93	−0.54
25d	OMe	1.951	19.68	20.74	24.82	54.78	14.00	29.95
26d	OMe	1.512	7.71	10.64	18.03	29.75	2.44	15.09
27d	OMe	1.383	13.15	15.68	15.69	23.14	17.84	20.28

[a] The distances R of C1−C1′ and C2−C2′, respectively, are also given. [b] B2PLYPD/6-31G*. [c] B2PLYPD/def2-TZVP//B2PLYPD/6-31G*. [d] DLPNO−CCSD(T)/def2-TZVP//B2PLYPD/6-31G*. [e] (12/10)CASSCF/6-31G*//B2PLYPD/6-31G*. [f] (12/10)CASPT2/6-31G*//B2PLYPD/6-31G*. [g] UB3LYP/6-31G*. [h] Optimization using UB3LYP/6-31G* leads to no converged minimum structure.

Before performing calculations on substituted phenylacetylenes, we wanted to test whether the dimerization can even be correctly calculated by the less time-consuming method UB3LYP/6-31G* using the simple benchmark systems **18a-**

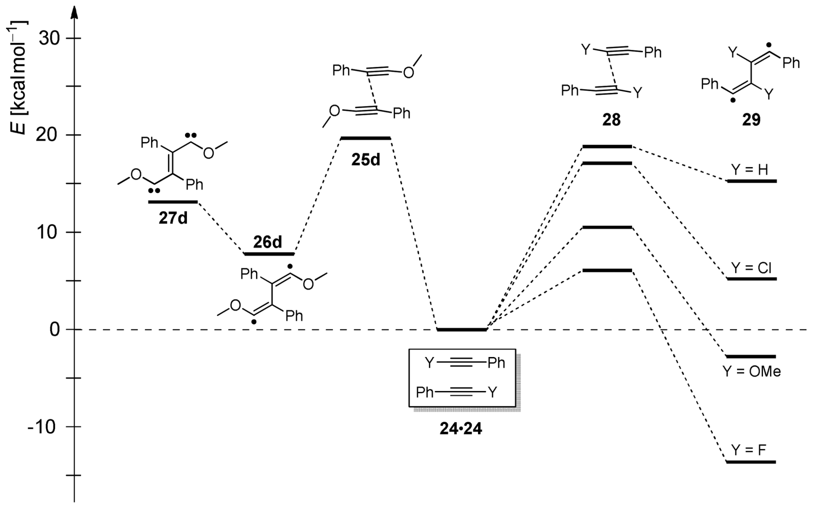


Figure 3. Energy profiles of the dimerization of substituted alkynes **24·24** to diradicals **26d** and **29** as well as to dicarbene **27d** calculated using B2PLYPD/6-31G*.

IV (Scheme 7, X = H, Y = OH) and **18d-I** (X = OH, Y = H). In Table 3, values obtained by UB3LYP/6-31G* are compared with those calculated with more accurate methods.

A comparison of the energy values shows that all selected methods lead to similar results, which means that the approximation UB3LYP/6-31G* should in principle be appropriate for the dimerization of phenyl-substituted alkynes **24** (Scheme 9).

In case of the alkynes **24b** and **24c**, the 1,1′ and 2,2′ dimerizations were already calculated by UB3LYP/6-31G*, and it was shown that 1,1′ dimerizations are more than 5 kcal/mol energetically preferred in comparison to the corresponding 2,2′ dimerizations.[22] Therefore, only the 1,1′ dimerizations were calculated for **24a–c**. These 1,1′ dimerizations lead to the diradicals **29a–c**, in which the phenyl rings are attached to the radical centers (Scheme 9). In the case of **24d**, the energy profile of the 2,2′ dimerization was also calculated because the OH group as a good π donor can stabilize both an adjacent radical center (**26d**) and a carbene (**27d**, see previous section).

The stationary points for the dimerizations of **24** were optimized by B2PLYPD/6-31G* and UB3LYP/6-31G* (Table 4). Additionally, single point calculations were performed on the geometrically optimized structures via B2PLYPD, (12/10)CASSCF,[33] (12/10)CASPT2,[34] and DLPNO–CCSD(T).[35] The 6-31G*[36] and def2-TZVP[37] basis sets were employed. While UB3LYP, B2PLYPD, and CCSD(T) are based on a single reference configuration, the methods CASSCF and CASPT2 can also describe degenerated correlation effects. This is extremely important for diradical states. Furthermore, the CASPT2 approximation considers dynamic correlation effects.

Several results for the dimerizations of **24** are summarized in Table 4 and in Figure 3. All methods used show the same tendency with respect to substituent Y: The nonsubstituted **24a** exhibits the highest activation barrier, followed by **24c**. Phenylfluoroacetylene (**24b**) is most reactive, while **24d** is situated between the fluoro and chloro derivatives, which is due to the electronegativity of the substituents as mentioned in the last section. The values obtained by the used methods differ significantly. As expected, the energies obtained from CASSCF calculations are too high because no dynamic correlation was taken into account. The energies for the transition states **28a–d** vary depending on the applied method (B2PLYPD, DLPNO–CCSD(T), (12/10)CASPT2, and UB3LYP) by 6–9 kcal/mol. The highest difference is found for the diradicals. The CASPT2 energies for the diradicals are 5–10 kcal/mol lower than the energies obtained by B2PLYPD. This can be ascribed to the effect that CASPT2 tends to overestimate the stabilizing energies of diradical states compared with closed shell systems.[14b,15,20] On the other hand, the DLPNO–CCSD(T) energies for the diradicals are about 10 kcal/mol higher than those obtained by B2PLYPD. Because both methods are based on a single reference configuration and cannot describe properly degenerated correlation effects, the obtained results for the diradicals should be handled with care.

An analysis of the CASSCF wave function allows the determination of the diradical character of the stationary points. As a measure of the diradical character of the transition states (**25d** and **28**) and the diradicals (**26d** and **29**), the occupation numbers of the frontier orbitals n_1 (antibonding linear combination) and n_2 (bonding linear combination) can be used (Figure 4 and Table 5).[38] In a perfect diradical, both frontier orbitals would be equally populated. A comparison shows that all stationary states are still far from being "perfect".

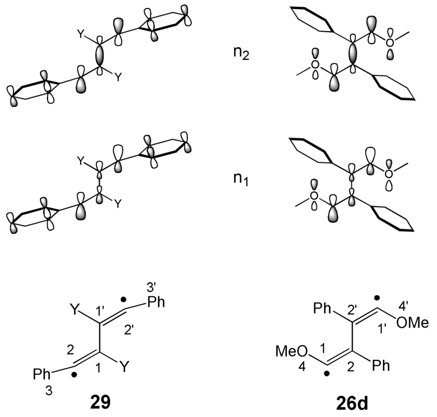


Figure 4. Schematic representation of the linear combinations of the nonbonding orbitals of the diradicals **26d** and **29**. The orbital n_1 represents the antibonding linear combination, whereas the orbital n_2 is the bonding linear combination. Please note the strong through-bond interaction in n_2.

Table 5. Occupation Numbers for the Linear Combinations of the Nonbonding Orbitals n_1 (Antibonding Linear Combination) and n_2 (Bonding Linear Combination) of 25d, 26d, 28, and 29[a]

	X	Y	n_1	n_2
28a	Ph	H	1.745	0.259
29a	Ph	H	1.351	0.651
28b	Ph	F	1.935	0.070
29b	Ph	F	1.486	0.517
28c	Ph	Cl	1.760	0.243
29c	Ph	Cl	1.441	0.562
28d	Ph	OMe	1.934	0.071
29d	Ph	OMe	1.360	0.643
25d	Ph	OMe	1.697	0.304
26d	Ph	OMe	1.294	0.706

[a] The results are taken from (12/10)CASSCF/6-31G*//B2PLYPD/6-31G* calculations.

The reason for that is a strong through-bond interaction[39] between the orbitals of the radical centers. Hence, the description of the transition states (**25d** and **28**) and the diradicals (**26d** and **29**) using a single reference method such as B2PLYPD is justified.

Moreover, the diradical character of **26d** is more distinct than that of **29d**. For the latter, an interaction between the radical centers and the orbitals of the phenyl group is possible, which also leads to a decrease of the diradical character (Figure 4).

Please note that the phenyl groups in **29** are rotated in such a way that the π orbitals of the aromatic units interact with the nonbonding orbitals of the radical center and not with the π orbitals of the butadiene unit (Figure 4). This interaction can also be recognized by the geometry of the radical center: For **29d**, the C1−C2−C3 angle amounts to 158°, which pleads for an sp- rather than for an sp^2-hybridized C2 atom. However, for **26d**, a C2−C1−O4 angle of 133° is found, which does not strongly deviate from the typical value for an sp^2-hybridized C1 atom.

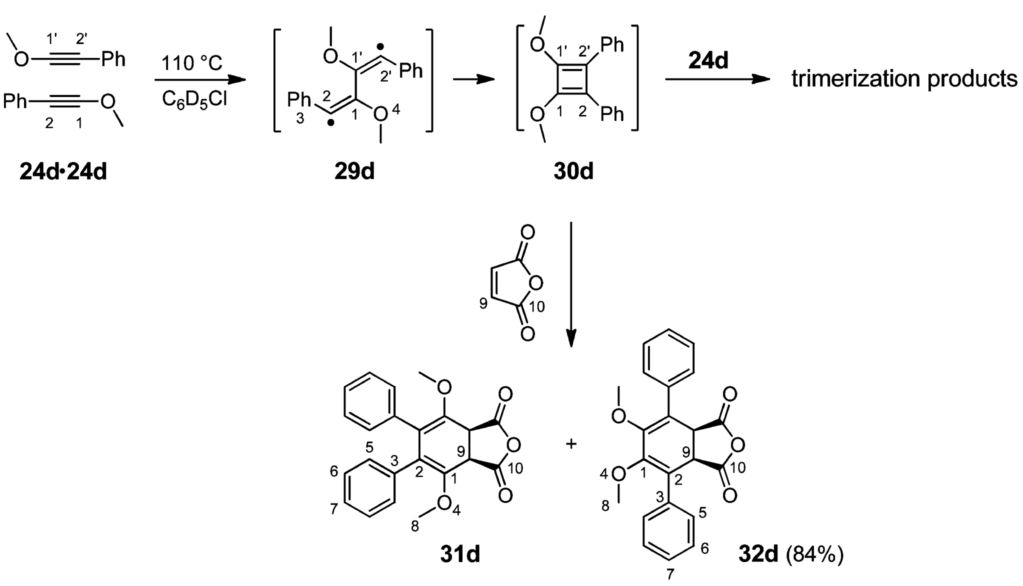
Trapping Experiments and Kinetic Studies. To verify the theoretical statements, we carried out thermal dimerization experiments with phenylmethoxyacetylene (**24d**). The methoxy compound was used because its reactivity is situated between the less reactive phenylchloro- (**24c**) and the highly reactive phenylfluoroacetylene (**24b**). Moreover, for this compound no investigations concerning thermal behavior were performed yet.

In the first step phenylmethoxyacetylene (**24d**) was heated in $C_2D_2Cl_4$ at 110 °C. After 65 h, conversion was almost complete (Figure S2, Supporting Information); however, a series of products that cannot be separated from each other was formed. The proposed reaction course is in the first step the formation of the diradical **29d**, which reacts to the energetically more stable cyclobutadiene **30d** (Scheme 10). According to B2PLYPD/6-31G*, the energy difference amounts to −36.6 kcal/mol in favor of cyclobutadiene **30d**. In a second step, cyclobutadiene **30d** reacts with unconverted phenylmethoxyacetylene (**24d**) to a trimerization product (Scheme 10). The reaction of a cyclobutadiene with an alkyne can proceed over a Diels−Alder reaction[40] or over diradical intermediates.[41,22] Therefore, it is not surprising that trimerization of **24d** leads to a multitude of products.

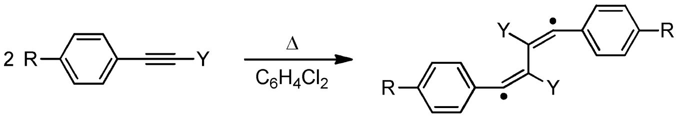
In order to trap the intermediately formed cyclobutadiene **30d** with high selectivity and in high yield, maleic anhydride (0.74 equiv) was added to the reaction mixture (Scheme 10). Maleic anhydride is known to be a very good dienophile for Diels−Alder reactions and should therefore be able to trap cyclobutadiene **30d** better than the electron-rich phenylmethoxyacetylene (**24d**). Diels−Alder reactions between a cyclobutadiene and an alkyne lead to a bicyclic compound, which is thermally rearranged to the corresponding cyclohexadiene system[40a] so that the anhydrides **31d** and **32d** are expected to be formed.

Dimerization of **24d** with subsequent trapping was carried out in C_6D_5Cl at 110 °C using a concentration of 10^{-2} M for **24d**. These conditions allow tracking the reaction course by NMR and determining the conversion and yield by internal standard (C_6HD_4Cl). After 65 h, 90% of phenylmethoxyacetylene (**24d**) was converted (Figure S3, Supporting Information). Referring to this conversion, the yield of the bicyclic system **32d** amounts to 84%. Conversion and yield are reproducible without problems, and the bicyclic compound

Scheme 10. Trapping Experiment of the Intermediately Formed Cyclobutadiene 30d with Maleic Anhydride as Dienophile



Scheme 11. Experimentally Determined and Calculated Activation Energies of the Dimerization of 24d–f to 29d–f[a]



				E_a(exp)	B2PLYPD	DLPNO-CCSD(T)	UB3LYP
24d	R = H, Y = OMe	**29d**	R = H, Y = OMe	16.8	11.7	15.5	16.3
24e	R = CH_3, Y = Cl	**29e**	R = CH_3, Y = Cl	21.9	17.0	24.4	21.7
24f	R = CH_3, Y = H	**29f**	R = CH_3, Y = H	--	21.7	28.3	21.1

[a] The geometric parameters were optimized using B2PLYPD/6-31G*. The energies were calculated by means of B2PLYPD/def2-TZVP, DLPNO–CCSD(T)/def2-TZVP, and UB3LYP/6-31G*.

can be separated from side products without difficulties. Two-dimensional NMR experiments prove that the obtained product is **32d** and not **31d** (Figures S11 and S12, Supporting Information).

To rule out that the bicyclic system **32d** is formed by the reaction of the diradical **29d** with maleic anhydride, phenylmethoxyacetylene (**24d**) was reacted with the acyclic *cis*-configured dimethyl maleate under similar conditions, and the reaction course was monitored by means of ^{1}H NMR spectroscopy. If the mechanism is a radical addition reaction, *cis*–*trans* isomerization would be observed in the products. The lack of substantial isomerization during the reaction (Figure S4, Supporting Information) is a hint for the formation of cyclobutadiene **30d** and a subsequent concerted addition process.

To compare the reaction behavior of phenylmethoxyacetylene (**24d**) with the nonsubstituted phenylacetylene (**24a**) and the chloro-substituted phenylacetylene **24c**, compounds **24a** and **24c** were also reacted with maleic anhydride in C_6D_5Cl at 110 °C. After 65 h, **24a** showed no dimerization products (Figure S5, Supporting Information), whereas a conversion of 40% was obtained for **24c** (Figure S6, Supporting Information). However, a multitude of compounds was generated, which points to the occurrence of radical trapping mechanisms.

To investigate the effect of the substituents in a quantitative way, the model compounds **24d–f** were used for kinetic studies (Scheme 11). The model compounds were heated in 1,2-dichlorobenzene at different temperatures, and the decay of the alkynes were determined by means of ^{1}H NMR spectroscopy. The methyl groups of **24e,f** in *para* position were needed for an easier determination of the concentration of the alkynes. Maleic anhydride was added to the solution to trap the intermediately formed cyclobutadienes, and cyclodecane was used as internal standard. Alkyne **24f** having a hydrogen atom bound to the triple bond showed no conversion even after 2 days at 175 °C. The plots of the reciprocal concentrations of the alkynes **24d,e** as a function of the reaction time reveal a clean second order behavior with respect to the alkynes (Figures S7–S10 and Table S10, Supporting Information). The Arrhenius plots for the dimerization of **24d,e** are shown in Figure 5. They yield activation energies of 16.8 ± 1.0 and 21.9 ± 1.1 kcal/mol for **24d** and **24e**, respectively. These values agree fairly well with the calculated energies (Scheme 11), whereby the best agreement is found for the data obtained by the DLPNO–CCSD(T) and UB3LYP approximations.

All experiments confirm the calculations with regard to reactivity dependent on the substituent Y: The methoxy-substituted phenylacetylene **24d** dimerizes much more easily than the chloro-substituted and the nonsubstituted phenylacetylene. Cyclobutadiene **30d** is formed as intermediate and can be trapped via Diels–Alder reaction.

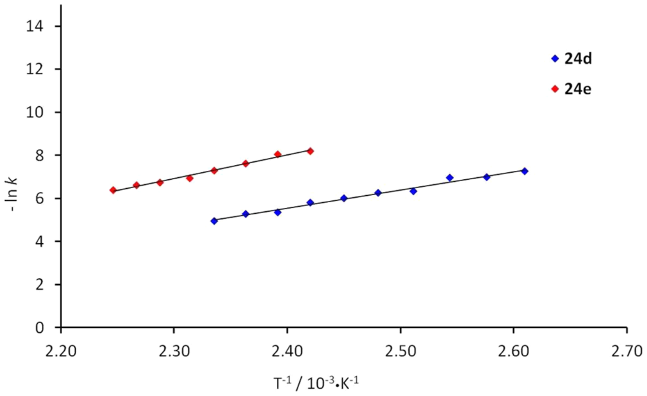


Figure 5. Arrhenius plots for the dimerization of **24d** (blue) and **24e** (red). E_a(**24d**) = 16.8 ± 1.0 kcal/mol (R = 0.991) and E_a(**24e**) = 21.9 ± 1.1 kcal/mol (R = 0.993).

■ CONCLUSION

In summary, we were able to show that the dimerization of substituted alkynes strongly depends on the substituents. For the investigated monosubstituted alkynes, the favorable dimerization is in general the one leading to bond formation at the nonsubstituted carbon atoms. Dicarbene formation was only observed if strong π donors like NH_2 and OH are attached to the carbene centers. The more electronegative the atom bound to the reaction center, the lower is the activation barrier and the reaction energy for diradical formation. For the examined substituents, the following series is found: F > OH > Cl, NH_2 > SH, H, CN. This series can be explained by the fact that electronegative elements (like fluorine, oxygen, or chlorine) have lower σ^*_{C-Y} orbitals than the nonsubstituted compound. Accordingly, the stabilizing interactions of the σ^* orbitals with the occupied antibonding linear combination ($n_{C2/C2'}$) are higher for diradicals having electronegative elements (like fluorine, oxygen, or chlorine) bound to C1. Afterward the dimerization of substituted phenylacetylenes was calculated by B2PLYPD, CASPT2, and DLPNO–CCSD(T). Even here it becomes evident that the reactivity of phenylacetylenes increases with higher electronegativity of the substituent, so that the following reactivity series is obtained: F > OCH_3 > Cl > H. With trapping experiments and kinetic studies, this series was confirmed. In the case of phenylmethoxyacetylene (Ph–C≡C–OCH_3), the yield of the cycloaddition product of the corresponding cyclobutadiene and maleic anhydride amounts to 84% of the converted acetylene. This makes the cyclization reaction attractive for a synthetic route to cyclohexadiene derivatives starting from alkynes.

COMPUTATIONAL DETAILS

All calculations were performed by using the program packages Gaussian 09,[42] MOLPRO,[43] and ORCA.[44] The geometrical parameters of the stationary points were optimized by means of B2PLYPD (for all) and UB3LYP (for **18a-IV**, **19a-IV**, **19d-I**, **20a-IV**, **20d-I**, **21d-I**, **24**, **25d**, **26d**, **27d**, **28**, and **29**). As basis sets, the aug-cc-pVDZ[17] and the 6-31G*[36] have been used. For all stationary points, no symmetry restriction was applied. Frequency calculations were carried out at each of the structures to verify the nature of the stationary point. It turned out that all transition states have exactly one imaginary frequency, whereas the alkynes, diradicals, and dicarbenes have none. The energies of the stationary points were calculated using CCSD(T),[18] DLPNO−CCSD(T),[35] (12/10)CASSCF,[33] and (12/10)CASPT2.[34] The 6-311++G(3d,2p),[19] the 6-31G*,[36] def2-TZVP,[37] and cc-pVTZ[17] basis sets were employed.

ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates and absolute energies for all calculated compounds, trapping of the cyclobutadienes with dienophiles, kinetic studies, data of the new compound, and complete references 42 and 43. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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