Orthoamides and iminium salts, LXXIII[1] Contributions to the cleavage of carboxylic acid orthoamides – a new access to *N,N,N',N'*-tetraalkyl-carboxamidinium salts

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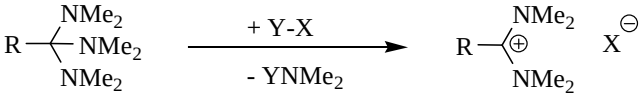
Dedicated to Rainer Beckert on the occasion of his 60th anniversary

Abstract



Orthoamides **7b-e** of alkyne carboxylic acids are transformed by benzoyl chloride to give the corresponding amidinium chlorides **13b-f**, which were isolated as the tetraphenylborates **14**. The reaction of the orthoamide derivative of phenylpropiolic acid **7a** with acetic acid anhydride results in the formation of the acylated ketene aminal **20**. The orthoamide of propiolic acid **22** and chloroform react, affording the vinylogous guanidinium salt **24**. By the hydrolysis of the orthoamide derivative of phenylpropiolic acid **7a** the *β*-keto-carboxylic acid amide **31A**, which is in equilibrium with its enol form **31B,** was obtained. Primary and secondary amines react with the phenylpropiolamidinium chloride **13a** under conjugated addition, delivering vinylogous guanidinium salts **33**.

Keywords: Orthoamides, alkyne carboxylic acids, cleavage reactions, amidinium salts

Introduction

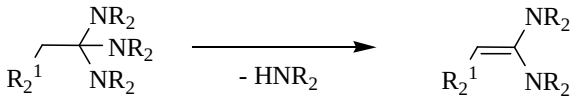
By definition three amino functionalities are linked to one carbon atom in an orthoamide group. The stability of orthoamides depends on one hand on the nature of the *N*-substituents and on the other hand on the degree of substitution in α-position to the orthoamide function.

Thus, no stable orthoamides are known to contain NH-alkyl-groups. Only orthoamides, possessing three acylamino groups like in tris(formylamino)methane (**1**), were found to be stable.[2] Orthoamides, in which the orthoamide function is set up by three dialkylamino groups like in tris(dimethylamino)methane (**2**), turned out also to be stable, isolable compounds.[3,4]

1 **2**

Scheme 1. Orthoamide derivates **1,2** of formic acid.

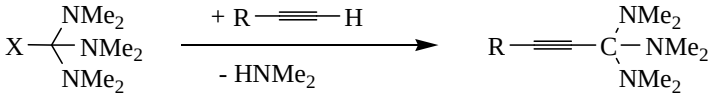
Stable orthoamides **3** possessing a CH-bond in α-position to the orthoamide function are not known. Obviously compounds of type **3** spontaneously can lose dialkylamine giving the corresponding ketene aminals **4**.



3 **4**

Scheme 2. Formation of ketene aminals **4** from orthoamides **3**.

This observation corresponds to the experience that amidinium salts with the same C,C-skeleton as **3** react to give ketene aminals on treatment with bases.[4] For this reason only orthoamides derived from formic, benzoic and phenylpropiolic acid became known from their first synthesis in 1966 until 1990. The compounds were obtained from formamidinium salts, guanidinium salts or *N*,*N*-dialkylformamides and metal amides.[5] The orthoamide of phenylpropiolic acid **7a** was prepared from the orthoamide derivative of carbonic acid **5** and phenylacetylene for the first time.[6] Further orthoamides derived from alkyne carboxylic acids were obtained from 1-alkynes and the ortho carbonic acid derivative **6**.[7]

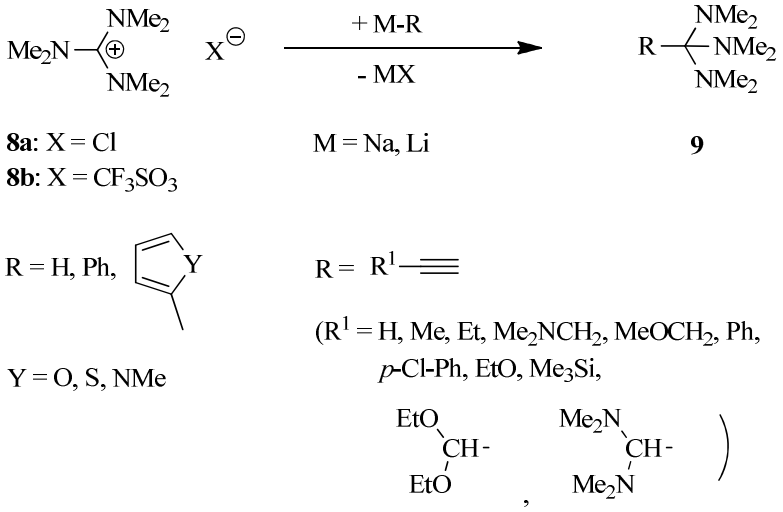


5: X = NMe_2
6: X = OC_2H_5

7a: R = Ph

Scheme 3. Orthoamides of alkyne carboxylic acids **7** from alkynes and orthocarbonic acid derivatives **5** and **6**.

With the aid of *N,N,N',N',N'',N''*-hexamethylguanidinium salts **8** orthoamide molecules **9** can be prepared easily since these salts react with complex hydrides as well as with metalorganic compounds to give the corresponding orthoamides **9**.[8-13]

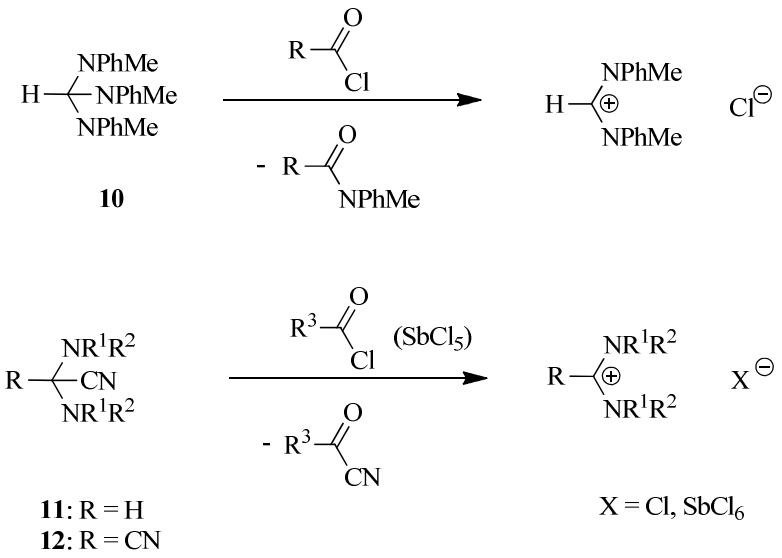


Scheme 4. Orthoamides **9** from guanidinium chloride **8a** and metalorganic compounds.

In conventional orthoamide synthesis an amide function is activated by electrophilic reagents. The iminium compounds thus formed are converted to amidinium salts which – as described above – can be transformed to the desired orthoamide compounds. In contrast to these methods, the orthoamide function is not constructed step by step. In the guanidinium salt procedure the orthoamide molecule is formed by a simple C,C-bond connecting reaction. As a consequence, orthoamides are now easily obtainable even with a quite complicated pattern of substituents. This prompted us to investigate if these new orthoamides can serve as starting materials for amidinium salts, which are not easily available by other methods.

Results and Discussion

Dialkylamino-methyleniminium salts are preparatively valuable reagents (Mannich reaction). For their preparation the cleavage of aminals by carboxylic acid chlorides is a standard procedure.[14] Little is known about related transformations of orthoamides and orthoamide derivatives. Tris(methylphenylamino)methane (**10**)[15] and bis(dialkylamino)acetonitriles **11**[16] and bis(dialkylamino)malononitriles **12**[17] react with carboxylic acid chlorides – if necessary in the presence of $SbCl_5$ – to give the corresponding amidinium salts.

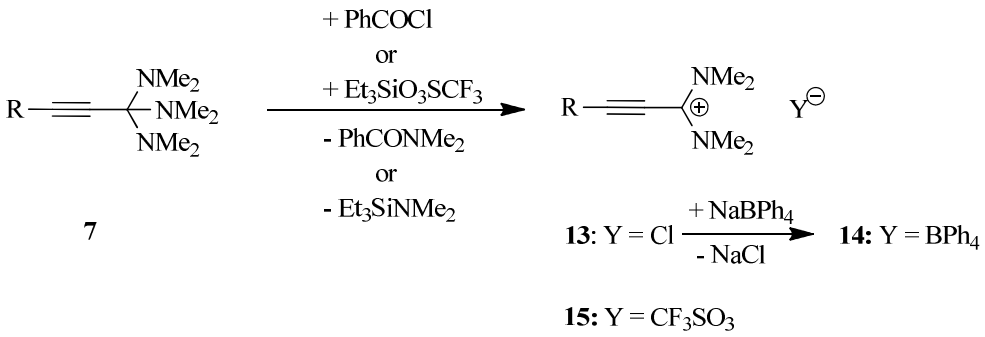


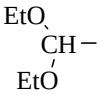
Scheme 5. Cleavage of orthoamide derivatives **10-12** by carboxylic acid chlorides.

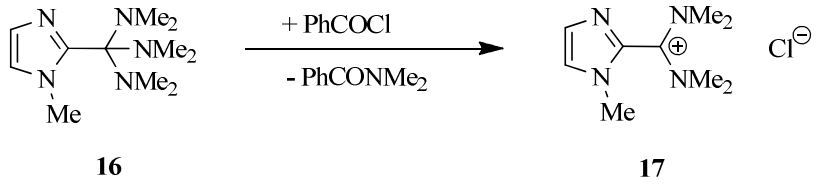
Cleavage of orthoamides with benzoyl chloride

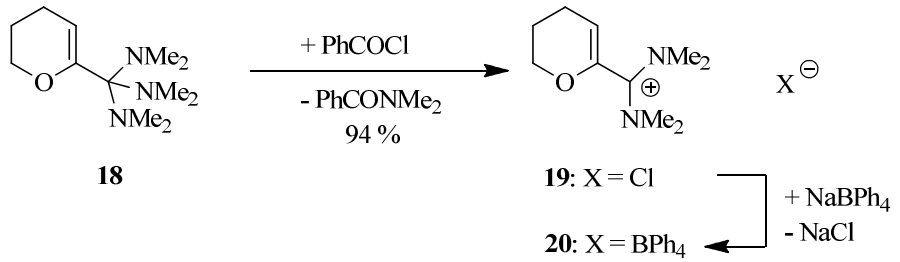
The preparation of derivatives of propiolamidinium salts by conventional methods was regarded to be not trivial for several reasons.[9,13] The cleavage of the corresponding orthoamides could deliver a solution for the problem. Indeed *N,N,N',N'*-tetramethyl-phenylpropiolamidinium chloride (**13a**) was prepared for the first time in pure state with 84% yield by the action of benzoyl chloride on 3,3,3-tris(dimethylamino)-1-phenyl-prop-1-yne.[9] Later on, a series of propiolamidinium salts could be obtained by the same procedure.[13] In these studies the very hygroscopic amidinium chlorides **13** were isolated as tetraphenylborates **14**. However, this method is not applicable for the cleavage of trialkylsilyl substituted alkynyl orthoamides.[13] In these cases triethylsilyl trifluoromethanesulfonate is the reagent of choice, which can be generally used for the transformation of orthoamides to the corresponding amidinium triflates **15**.[13] Trimethylsilyl halides are not as effective in orthoamide cleavage reactions as trialkylsilyl triflates.[13]

The preparation of imidazole-2-carboxamidinium salts of type **17**, starting from imidazole-2-carboxamides seems also to be difficult, according to established procedures, since the electrophilic reagents usually used for the activation of the amide function, would very likely attack the nitrogen atoms of the imidazole system. However, the imidazole-2-carboxamidinium salt **17** could be prepared from the corresponding orthoamide derivative **16** and benzoyl chloride.[12] We now found that the dihydro-4*H*-pyrane-carboxamidinium salt **19** can be obtained from the orthoamide derivate **18** by the same procedure. The chloride **19** was converted into the tetraphenylborate **20** for analytical characterization.



7, 13, 14, 15	a	b	c	d	e	f	g	h
R	Ph	Me	Et			EtO	Me_3Si	Me_2NCH_2
13: yield (%)	89	91	99	92	80			





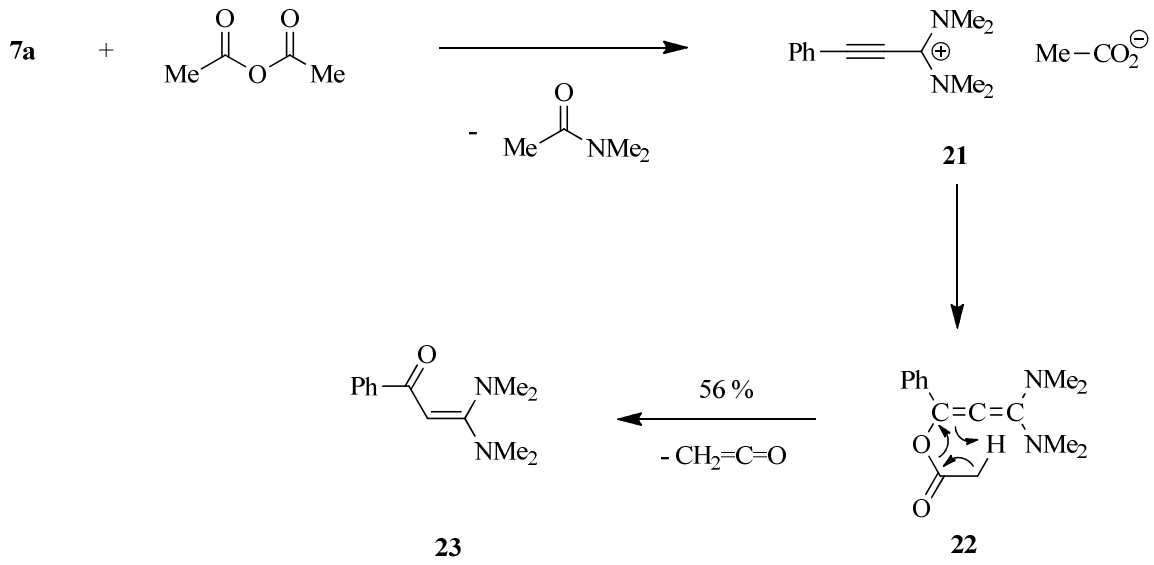
Scheme 6. Cleavage of orthoamides of alkyne carboxylic acids **7** by benzoyl chloride.

In order to evaluate the scope of this method we reacted the earlier described[7,9,20] orthoamides **7b**–**h** with benzoylchloride in ether. From the orthoamides **7b**–**d** the strongly hygroscopic corresponding amidinium chlorides **13b**–**d** could be obtained, which were isolated as tetraphenylborates **14b**–**d**. The amidinium chloride **13e** forms extremely hygroscopic colorless crystals, which could be characterized by NMR. A further characterization as a tetraphenylborate by elemental analysis was not possible, since the tetraphenylborate **14e**, prepared from **13e** could not be obtained in crystalline state. From the reactions of the orthoamides **7f**–**h** with benzoyl chloride resulted tarry products in which the presence of the guanidinium chloride **8a** could be detected. Obviously, these orthoamides are cleaved by another, hitherto unknown mechanism.

This deviating reaction path is observed when the substituent pattern of the substrate **7** does not fit to the cleaving reagent. Thus the orthoamide **7g** is not converted into the corresponding amidinium chloride **13g** by benzoylchloride, however, the treatment of **7g** with triethylsilyl triflate affords the salt **15g**.[13]

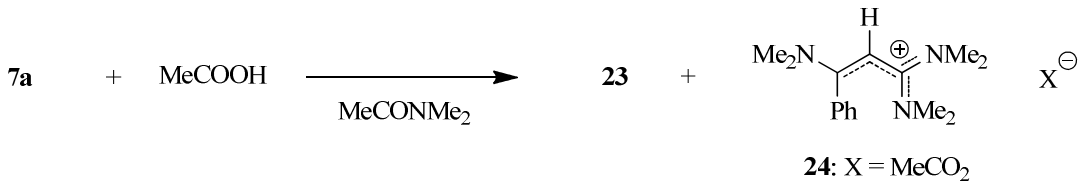
Cleavage of the orthoamide 7a by acetic acid anhydride

We tried to cleave the orthoamides **7a** and **25** by other reagents. From the results of these reactions we expected to get insight into side reactions which can compete with the cleavage of the orthoamide function. When **7a** was treated with acetic acid anhydride in excess, we obtained with 63% yield a yellowish distillable oil, which turned out to be the ketene aminal **23**.



Scheme 7. Cleavage of 1,1,1-tris(dimethylamino)-3-phenyl-2-propyne **(7a)** by acetic acid anhydride.

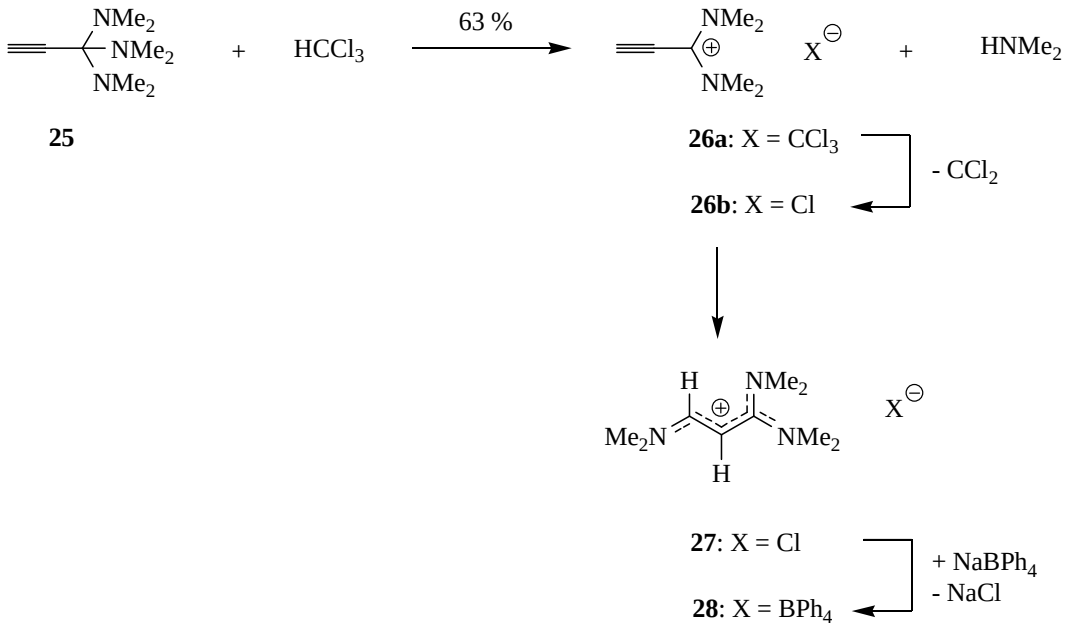
The formation of the ketene aminal **23** can be explained in the following way. In the first step the amidinium acetate **21** is formed from **7a** and acetic acid anhydride. The addition of the acetate ion on the triple bond of the phenylpropiolamidinium ion affords the allene **22**, which delivers the ketene aminal **23** by elimination of ketene. The result of this cleavage reaction reminds of the known acetolysis of **7a** which also affords the ketene aminal **23** as main product. The acrylamidinium salt **24** was isolated as a side product. The allene **22** was assumed to be an intermediate[6] in explaining the formation of the reaction products.



Scheme 8. Cleavage of 1,1,1-tris(dimethylamino)-3-phenyl-2-propyne **(7a)** by acetic acid.

Cleavage of the orthoamide 25 by chloroform

It is well known that hydrogen chloride can be abstracted from chloroform by strong bases delivering dichlorocarbene via α-elimination. Assuming that the orthoamide **25** can produce dichlorocarbene from chloroform, the hydrogen chloride formed should cleave the orthoamide function of **25** to give the propiolamidinium salt **26a**, which we expected to be trapped by the trichloromethyl-anion formed from chloroform. After stirring **25** in chloroform for 24 h at room temperature, the chloroform was removed in vacuo. The residual yellow oil crystallized on treatment with diethylether. After recrystallization from acetonitrile/ethyl acetate, a colorless hygroscopic salt with mp 186-187 °C resulted. This could be identified as the hygroscopic vinylogous guanidinium chloride **27**, which was transformed into the slightly hygroscopic tetraphenylborate **28**.



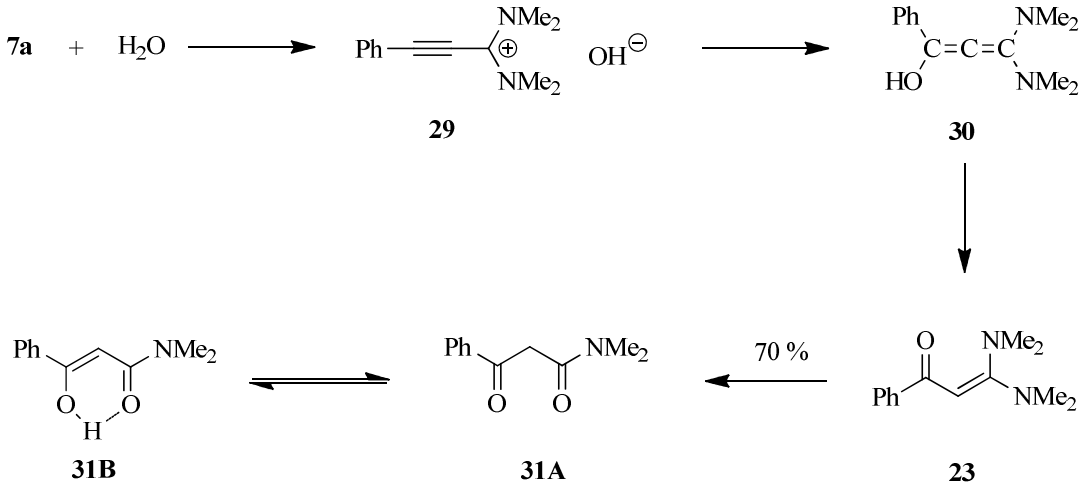
Scheme 9. Cleavage of 1,1,1-tris(dimethylamino)-2-propyne **(25)** by chloroform.

For the trichloromethyl anion in **26a,** two reaction paths exist. On one hand it can add on the propiolamidinium ion, on the other hand it can lose a chloride ion forming dichlorocarbene. Very

likely, the addition of the trichloromethyl anion on the propiolamidinium ion is reversible. Thus in equilibrium trichlormethyl anions are always present, which are completely decomposed to chloride ions and dichlorocarbene in the end. So finally, the salt **26a** is completely converted into the salt **26b**, on which dimethylamine can add to give the salt **27**.

Hydrolysis of the orthoamide 7a

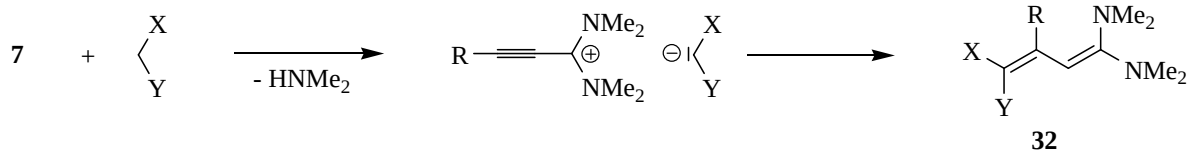
Since nothing is known on the hydrolysis of orthoamides **7** we heated **7a** with diluted sodium hydroxide solution for 2 h under reflux. The reaction mixture was neutralized with diluted HCl and then extracted with dichloromethane. After further work up procedures we obtained colorless crystals with mp 75-77 °C with 72% yield which were identified as *N*,*N*-dimethyl-2-benzoylacetamide (**31A**) in equilibrium with the corresponding **Z**-enol-isomer **31B**. The compound forms an intensive red-violet colored iron complex when an aqueous solution of iron-III-chloride is added to a methanol solution of **31**. The compound **31A** was prepared by Oishi and Ochiai by benzoylation of *N*,*N*-dimethylacetamide dimethylacetal.[18]



Scheme 10. Hydrolysis of 1,1,1-tris(dimethylamino)-3-phenyl-2-propyne **(7a)**.

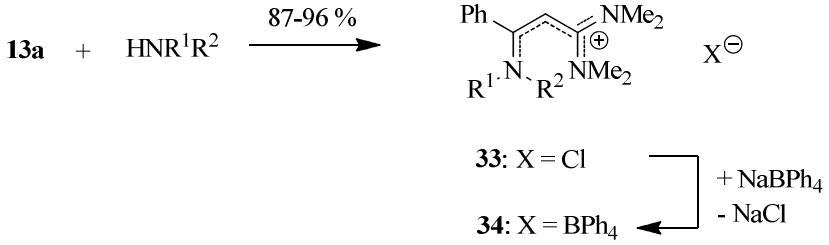
The propiolamidinium hydroxide **29** is probably formed in the first step from **7a** and water. Addition of the hydroxide ion gives the enol **30** which tautomerizes to afford the ketene aminal **23,** which in turn delivers the keto/enol-mixture **31A**, **31B** on hydrolysis.

Butadiene derivates **32** are mainly obtained as reaction products from condensation reactions of orthoamides **7** with CH_2-acidic compounds.[11,12,19] These results were explained by the assumption that in the first step propiolamidinium ions and carbanions are formed from the starting compounds by loss of dimethylamine. The ketene aminals **32** result from the ionic species thus formed via conjugated addition.



Scheme 11. Condensation reactions of orthoamide derivatives **7** with CH_2-acidic compounds.

The propiolamidinium salt **13a** can be prepared in pure state.[9] So it was possible to confirm that nucleophiles enter propiolamidinium salts in 3-position. When the chloride **13a** was treated with butylamine and secondary amines, the reaction products were the very hygroscopic 3-amino-acrylamidinium chlorides **33**, isolated as the tetraphenylborates **34**. The compound **34d** is known. It was obtained directly from the tetraphenylborate **14a** and morpholine.[13]



33, 34	a	b	c	d
R^1	H	Et	$(CH_2)_5$	$(CH_2)_2O(CH_2)_2$
R^2	Bu	Et		

Scheme 12. Addition of amines onto the phenylpropiolamidinium salt **13a**.

Conclusions

The present investigations have enlarged the number of methods for the cleavage of orthoamide functions in orthoamides of alkyne carboxylic acids. Thus further examples have been reported for the transformation of orthoamides **7b**–**d** to propiolamidinium salts **13** and **14** resp. by benzoyl chloride. The method is not applicable for the cleavage of orthoamides **7e**–**h** since in these orthoamides additional functional groups are present, which can induce undesired side reactions. The reaction of **7a** with acetic acid anhydride demonstrates that orthoamides as **7a** can be converted for example to acylated ketene aminals as **23**. The orthoamide group in **25** is cleaved by chloroform even at room temperature to give the vinylogous guanidinium salt **27**. Thus the NMR spectra of orthoamides should not be recorded in chloroform solutions. The hydrolysis

reaction of an orthoamide of compound type **7** has been reported for the first time. The β-keto-carboxylic acid amide **31** was isolated as reaction product.
In total it could be shown that the orthoamides **7** can serve as starting materials for the preparation of amidinium salts of alkyne carboxylic acids, acylketene aminals, vinylogous guanidinium salts and β-keto-carboxylic acid amides.

Experimental Section

General. Melting points were measured with a Büchi 510 apparatus. IR spectra were recorded on a Perkin Elmer Spectrometer 457. ^{1}H-NMR spectra were recorded with a Varian T60 (60 MHz), a Bruker WP80 (90 MHz) and a Bruker AMX500 (500 MHz) spectrometer. ^{13}C NMR spectra were recorded with a Bruker AMX500 (125 MHz) spectrometer. Solvents were dried by standard procedures. All reactions – except the hydrolysis reaction – were performed under exclusion of moisture (KOH) drying tubes.

Cleavage of orthoamides 7 with benzoyl chloride – general procedure
A solution of the corresponding orthoamide **7** in dry diethylether was added dropwise with stirring to a solution of benzoylchloride in dry diethylether under cooling with ice. After 0.5-1 h stirring, the precipitated salt was filtered off in vacuo with exclusion of moisture. The hygroscopic colorless salts were dried in an oil-pump vacuum. From not too extreme hygroscopic products NMR-spectra could be recorded. In other cases the crude product was dissolved in dry acetonitrile. An equimolar amount of sodium tetraphenylborate in dry acetonitrile was added to this solution. The mixture was boiled for a short time and then freed from the sodium chloride by filtration of the hot solution. The filtrate was concentrated in a rotatory evaporator. The precipitated crystals were isolated by filtration and recrystallized from dry acetonitrile. Preparation procedures are described for all orthoamide derivatives **7a,**[6,7,9] **7b-h**[20] and **18**[9] which were used in the present study.

***N,N,N',N'*-Tetramethyl-5,6-dihydro-4*H*-pyrane-2-carboxamidinium tetraphenylborate (20).** According to the general procedure 4.70 g (94%) of crude **19** were isolated from 5.2 g (23 mmol) 2-[tris(dimethylamino)methyl]-5,6-dihydro-4*H*-pyrane (**18**) in 30 ml Et_2O and 3.22 g (23 mmol) benzoyl chloride in 30 ml Et_2O. **19** was converted to the tetraphenylborate **20**, colorless crystals, mp 174 °C. **19**: ^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ = 1.75-2.50 [m, 4H, $(CH_2)_2$], 3.41 (s, 12H, NMe_2), 4.16 (t, *J* = 6 Hz, 2H, OCH_2), 5.90 (t, *J* = 4 Hz, CH) ppm. **20**: IR (KBr) ν (cm^{-1}): 1620 ($C=N^+$). ^{1}H NMR (90 MHz, [D_6] DMSO, TMS): δ = 1.62-2.30 [m, 4H, $(CH_2)_2$], 3.07 (s, 12H, NMe_2), 4.07 (t, *J* = 6 Hz, 2H, OCH_2), 5.64 (t, *J* = 4 Hz, CH), 6.65-7.40 (m, 20H, ArH) ppm. Anal. Calcd. for $C_{34}H_{39}BN_2O$ (502.48): C, 81.27; H, 7.82; N, 5.57%. Found: C, 81.70; H, 7.79; N, 5.48%.

***N,N,N',N'*-Tetramethyl-but-2-yne-amidinium tetraphenylborate (14b).** From 3.90 g (21 mmol) 1,1,1-tris(dimethylamino)-2-butyne (**7b**) in 30 ml Et_2O and 3.00 g (21 mmol) benzoyl chloride were obtained 3.40 g (91%) of crude **13b**, which were transformed to the tetraphenylborate **14b**, colorless crystals with mp 165 °C; IR (KBr): ν (cm^{-1}): 2278, 2242 (C≡C), 1640 ($C=N^+$). ^1H NMR (90 MHz, [D_6]DMSO, TMS): δ = 2.15 (s, 3H, Me), 3.12 (s, 12H, NMe_2), 6.50-7.52 (m, 20H, ArH) ppm. Anal. Calcd. for $C_{32}H_{35}BN_2$ (458.43): C, 83.83; H, 7.70; N, 6.11%. Found: C, 83.69; H, 7.65; N, 6.19%.

***N,N,N',N'*-Tetramethyl-pent-2-yne-amidinium tetraphenylborate (14c).** From 6.10 g (31 mmol) 1,1,1-tris(dimethylamino)-2-pentyne (**7c**) in 40 ml diethylether and 4.35 g (31 mmol) benzoylchloride in 30 ml diethylether (reaction time 30 min) were obtained 5.80 g (99%) of the crude chloride **13c**, which was converted to the tetraphenylborate **14c**, colorless crystals, mp 138 °C. **13c**: ^1H NMR (90 MHz, $CDCl_3$, TMS): δ = 1.30 (t, *J* = 7 Hz, 3H, Me), 2.60 (q, *J* = 7 Hz, 2H, CH_2), 3.51 (s, 12H, NMe_2). **14c**: IR (KBr) ν (cm^{-1}): 2240 (C≡C), 1619 ($C=N^+$). ^1H NMR (90 MHz, [D_6] DMSO, TMS): δ = 1.12 (t, *J* = 7 Hz, 3H, Me), 2.52 (q, *J* = 7 Hz, 2H, CH_2), 3.10 (s, 12H, NMe_2), 6.57-7.50 (m, 20H, ArH) ppm. Anal. Calcd. for $C_{33}H_{37}BN_2$ (472.46): C, 83.89; H, 7.89; N, 5.93%. Found: C, 84.06; H, 7.92; N, 5.90%.

***N,N,N',N'*-Tetramethyl-4-methyl-pent-2-yne-4-ene-amidinium tetraphenylborate (14d).** Following the general procedure from 4.90 g (22.4 mmol) 5,5,5-tris(dimethylamino)-2-methyl-1-pentene-3-yne (**7d**) in 30 ml Et_2O and 3.30 g (23.5 mmol) benzoyl chloride in 40 ml Et_2O (reaction time 1 h) were isolated 4.5 g (92%) of crude **13d** which was transformed to the tetraphenylborate **14d**. To obtain an analytical pure compound with mp 130 °C **14d** had to be recrystallized 4 times from acetonitrile.
13d: ^1H NMR (90 MHz, $CDCl_3$, TMS): δ = 1.97 (s, 3H, Me), 3.55 (s, 12H, NMe_2), 5.70 (s, 2H, CH_2) ppm. **14d**: IR (KBr): ν (cm^{-1}): 2220 (C≡C), 1520 ($C=N^+$). ^1H NMR (90 MHz, [D_6]DMSO, TMS): δ = 2.20 (s, 3H, Me), 3.12 (s, 12H, NMe_2), 5.82 (s, 2H, CH_2), 6.63-7.30 (m, 20H, ArH) ppm. Anal. Calcd. for $C_{34}H_{37}BN_2$ (484.50): C, 84.29; H, 7.70; N, 5.78%. Found: C, 83.89; H, 7.72; N, 5.92%.

***N,N,N',N'*-Tetramethyl-4,4-diethoxy-but-2-yne-amidinium chloride (13e).** From 3.60 g (13.3 mmol) 4,4-diethoxy-1,1,1-tris(dimethylamino)-2-butyne (**7e**) and 1.86 g (13.3 mmol) benzoyl chloride were obtained 2.80 g (80%) of crude **13e** which could not be transformed to a crystalline tetraphenylborate **14e**.
13e: IR (KBr): ν (cm^{-1}): 2190 (C≡C), 1625 ($C=N^+$). ^1H NMR (90 MHz, $CDCl_3$, TMS): δ = 1.25 (t, *J* = 7 Hz, 6H, Me), 3.00 (q, *J* = 7 Hz, 4H, OCH_2), 3.54 (s, 12H, NMe_2), 5.48 (s, 1H, CH) ppm.

Cleavage of 3,3,3-tris(dimethylamino)-1-phenyl-prop-2-yne (7a) with acetic acid anhydride. 4.9 g (20 mmol) **7a** were added to 30 ml of acetic acid anhydride in small portions with stirring under cooling. The mixture was set aside for 18 h at ambient temperature. The excessive acetic

acid anhydride was distilled off in vacuo (20 Torr) and the residue destilled through a 15 cm Vigreux-column with fractionation. Yield: 2.5 g (56%) 3,3-bis(dimethylamino)-1-phenyl-prop-2-enone (**20**), yellowish oil, bp 145 °C/0.001 Torr Lit.[6]: 143 °C/0.2 mm.

Reaction of 3,3,3-tris(dimethylamino)propyne (25) with chloroform. A solution of 3.0 g (17.7 mmol) **25** in 30 ml dry chloroform was stirred 24 h at ambient temperature. After removal of the chloroform in a rotatory evaporator a slightly brown colored solid which was re-crystallized from ethyl acetate/acetonitrile (4:1) was obtained. Yield: 2.3 g (63%) *N*,*N*,*N'*,*N'*-tetramethyl-3-dimethylamino-prop-2-ene-amidinium chloride (**27**), colorless hygroscopic crystals, mp 186-189 °C.
^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ = 3.0, 3.16, 3.43 (s, 18H, NMe_2), 4.30 (d, *J* = 13 Hz, 1H, CH), 8.20 (d, *J* = 13 Hz, CH) ppm. Anal. Calcd. for $C_9H_{20}ClN_3$ (205.71): C, 52.55; H, 9.80; N, 20.42%. Found: C, 52.21; H, 10.02; N, 20.71%.

Tetraphenylborate (28). To a solution of 1.23 g (6 mmol) **27** in 20 ml acetonitrile was added a solution of 2.05 g (6 mmol) sodium tetraphenylborate in 10 ml acetonitrile. The mixture was heated for a short period of time and then filtered. The filtrate was evaporated and the residue washed with 30 ml diethylether. Yield: 2.47 g (84%) **28**, colorless crystals, mp 157-158 °C.
^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ = 2.83, 2.90, 3.03 (s, 18H, NMe_2), 4.26 (d, *J* = 13 Hz, 1H, CH), 6.7-7.4 (m, 21H, ArH and CH) ppm. ^{1}H NMR (500.1 MHz, [D_6]DMSO): δ = 2.81, 3.06 (s, 6H, NMe_2), 2.88 (s, 12H, NMe_2), 4.36 (d, $^3J_{HH}$ = 12.5 Hz, 1H, =CH), 6.75-6.85 (m, 4 H, BArH), 6.89-6.99 (m, 8 H, BArH), 7.17-7.28 (m, 8 H, BArH), 7.40 (d, $^3J_{HH}$ = 12.5 Hz, 1H, =CH) ppm. ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 36.9, 41.4, 44.7 (NMe_2), 81.4 (CH), 121.5, 121,7, 125.3 (q, *J* = 2.5 Hz, BCC_{Ph}), 135.5, 135.3 (ArC), 157.3 (CH-NMe_2), 163.7 (m_c, BC), 169.8 [$^+C(NMe_2)_2$] ppm. Anal. Calcd. for $C_{33}H_{40}BN_3$ (489.49): C, 80.97; H, 8.24; N 8.56%. Found: C, 80.81; H, 8.31; N, 8.26%.

Alkaline hydrolysis of the orthoamide derivative 7a. A mixture of 9.6 g (40 mmol) **7a** and 50 ml 1M sodiumhydroxide solution in water was heated to reflux for 2 h. The clear solution was neutralized with diluted hydrochloric acid and extracted 6 times with dichloromethane (30 ml). The combined extracts were dried with Na_2SO_4 and evaporated. The residue was a yellowish oil, which solidified after a short time. The compound was recrystallized from methanol/water (1:3). Yield: 5.7 g (72%) mixture of *N*,*N*-dimethyl-3-phenyl-3-oxo-propionamide (**31A**) and *N*,*N*-dimethyl-3-hydroxy-3-phenyl-acrylamide **31B**, mp 75-77 °C Lit.[18]: mp 84-85 °C.
Keto-isomer (**31A**): ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ = 3.10, 3.15 (s, 6H, NMe_2), 4.20 (s, 2H, CH_2), 7.4-8.3 (m, 5H, ArH).
Enol-isomer (**31B**): ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ = 3.10, 3.15 (s, 6H, NMe_2), 5.93 (s, 6H, CH), 7.4-8.3 (m, 5H, ArH), 15.55 (s, 1H, OH) ppm. Anal. Calcd. for $C_{11}H_{13}NO$ (191.23): C, 69.09; H, 6.85; N, 7.32%. Found: C, 69.03; H, 6.83; N, 7.27%.

Addition of amines to *N,N,N',N'*-tetramethyl-3-phenyl-propiolamidinium-chloride (13a) – general procedure. The corresponding amine (2.1 mmol) was added slowly to a solution of 0.5 g (2.1 mmol) **13a** in 20 ml acetonitrile. After 15-20 min a solution of 0.68 g (2.1 mmol) sodium tetraphenylborate in 10 ml acetonitrile was added. The mixture was heated upto 70 °C and filtered hot. The filtrate was evaporated. Treatment of the residual oily or solid compounds with diethylether afforded crystalline compounds, which were isolated by filtration.

***N,N,N',N'*-Tetramethyl-3-butylamino-3-phenyl-prop-2-ene-amidinium tetraphenylborate (34a).** From 0.15 g butylamine: yield 1.08 g (87%) **34a** slightly yellowish crystals, mp 185-155 °C.
^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ = 0.75-1.05 (m, 3H, CH_3), 1.1-1.6 [m, 4H, $(CH_2)_2$], 2.28 (s, 12H, NMe_2), 2.8-3.0 (m, 2H, NCH_2), 4.08 (s, 1H, CH), 4.1-4.3 (br s, 1H, NH), 6.7-7.6 (m, 25H, ArH) ppm. ^{1}H NMR (500.1 MHz, $[D_6]$DMSO): δ = 0.92 (t, *J* = 7.3 Hz, 3H, CH_3), 1.39-1.41 (m, 2H, CH_2), 1.62-1.65 (m, 2H, CH_2), 2.59 (s, 12H, NMe_2), 3.24-3.34 (m, 2H, NCH_2), 4.50 (s, 1H, =CH), 6.72-6.85 (m, 4H, ArH), 6.85-7.00 (m, 8H, ArH), 7.10-7.25 (m, 8H, ArH), 7.25-7.39, 7.40-7.55 (m, 5H, ArH) ppm. ^{13}C NMR (125.8 MHz, $[D_6]$DMSO): δ = 13.7 (CH_3), 19.8 (CH_2), 24.5 (CH_2), 40.1, 41.06, 41.3 (NMe_2), 43.7 (NCH_2), 80.3, 85.9 (CH), 121.5 (ArC), 125.29 (q, $^3J_{BC}$ = 2.5 Hz, ArC), 128.3, 128.5, 129.1, 130.5, 130.9, 134.3, 135.3, 135.6, 136.0 (Ar-C), 163.4 (m_c, B-C), 166.0 [$^+C(NMe_2)_2$], 169.6, 169.86 (=C-CH) ppm. Anal. Calcd. for $C_{41}H_{48}BN_3$ (607.63): C, 82.95; H, 8.15; N, 7.07%. Found: C, 83.01; H, 8.25; N, 7.15%.

***N,N,N',N'*-Tetramethyl-3-diethylamino-3-phenyl-prop-2-ene-amidinium tetraphenylborate (34b).** From 0.15 g diethylamine: yield 1.1 g (88%) **34b**, colorless crystals, mp 156 °C. ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ = 1.15 (t, *J* = 7 Hz, 6H, CH_3), 2.63 (s, 12H, NMe_2), 3.30 (q, *J* = 7 Hz, 4H, NCH_2), 4.58 (s, 1H, CH), 6.70-7.55 (m, 25H, ArH) ppm. ^{1}H NMR (500.2 MHz, $[D_6]$DMSO): δ_H = 0.85-1.40 (m, 6H, CH_3), 2.63 (s, 12H, NMe_2), 2.90-3.10 (m, 2H, NCH_2), 3.30-3.60 (m, 2H, NCH_2), 4.67 (s, 1H, =CH), 6.70-6.85 (m, 4H, ArH), 6.85-7.00 (m, 8H, ArH), 7.18-7.26 (m, 8H, ArH), 7.26-7.39 (m, 2H, ArH), 7.40-7.55 (m, 3H, ArH) ppm. ^{13}C NMR (125.8 MHz,$[D_6]$DMSO): δ = 11.3, 13.4 (CH_3), 41.2 (NMe_2), 43.7, 45.40 (NCH_2), 86.1 (=CH), 121.4, 125.1, 125.2, 128.5, 130.2, 134.7, 135.4 (ArC), 163.3 (m_c, B-C), 164.1 [$^+C(NEt_2)_2$], 169.7 (C=CH) ppm. Anal. Calcd. for $C_{41}H_{48}BN_3$ (607.63): C, 82.95; H, 8.15; N, 7.07%. Found: C, 83.15; H, 8.10; N, 7.18%.

***N,N,N',N'*-Tetramethyl-3-phenyl-3-piperidino-prop-2-ene-amidinium-tetraphenylborate (34c).** From 0.18 g piperidine: yield 1.1 g (96%) **34c**, colorless crystals, mp 186-198 °C. ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ = 1.68 [m, 6H, $(CH_2)_3$], 2.72 (s, 12H, NMe_2), 3.35 (m, 4H, NCH_2), 4.76 (s, 1H, CH), 6.90-7.80 (m, 25H, ArH) ppm. ^{1}H NMR (500.2 MHz, $[D_6]$DMSO): δ = 1.45-1.70 (m, 6H, CH_2), 2.63 (s, 12H, NMe_2), 3.10-3.40 (m, 4H, NCH_2), 4.77 (s, 1H, =CH), 6.75-6.84 (m, 4H, ArH), 6.85-6.98 (m, 8H, ArH), 7.12-7.25 (m, 8H, ArH), 7.26-7.38 (m, 2H, ArH), 7.45-7.57 (m, 3H, ArH) ppm. ^{13}C NMR (125.8 MHz, $[D_6]$DMSO): δ = 13.1 (CH_2), 23.5,

25.2 (CH_2), 41.3 (NMe_2), 50.0 (NCH_2), 87.2 (=CH), 121.4, 125.1 (q, $^3J_{B,C}$ = 2.5 Hz), 128.7, 130.6, 134.7, 135.4 (ArC), 163.3 (m_c, B-C), 165.4 [$^+C(NMe_2)_2$], 169.7 (C=CH) ppm. Anal. Calcd. for $C_{42}H_{48}BN_3$ (605.66): C, 83.29; H, 7.99; N, 6.93%. Found: C, 83.31; H, 8.11; N, 6.92%.

***N,N,N',N'*-Tetramethyl-3-morpholino-3-phenyl-prop-2-ene-amidinium-tetraphenylborate (34d).** From 0.18 g morpholine: yield 1.2 g (94%) **34d**, colorless crystals, mp 179-180 °C, Lit. [13]: mp 181-182 °C. ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ = 2.75 (s, 12H, NMe_2), 3.30, 3.80 [m, 8H, $(CH_2)_2$], 4.72 (s, 1H, CH), 6.90-7.80 (m, 25H, ArH) ppm. ^{1}H NMR (500.2 MHz, [D_6]DMSO): δ = 2.66 (m_c, 12H, NMe_2), 3.34 (bs, 4H, NCH_2), 3.66 (bs, 4H, OCH_2), 4.81 (s, 1H, =CH), 6.78-6.85 (m, 4H, ArH), 6.85-7.80 (m, 8H, ArH), 7.10-7.25 (m, 8H, ArH), 7.28-7.40 (m, 2H, ArH), 7.45-7.60 (m, 3H, ArH) ppm. ^{13}C NMR (125.8 MHz, [D_6]DMSO): δ = 41.3, 41.5 (NMe_2), 49.2 (NCH_2), 65.6 (OCH_2), 88.8 (=CH), 125.1, 125.3 (q, $^3J_{B,C}$ = 2.5 Hz), 128.9, 129.0, 130.8, 134.1, 135.5 (ArH), 163.3 (m_c, B-C), 165.3 [$^+C(NMe_2)_2$], 169.6 (C=CH) ppm. Anal. Calcd. for $C_{41}H_{46}BN_3O$ (607.63): C, 81.04; H, 7.63; N, 6.91%. Found: C, 80.93; H, 7.73; N, 6.92%.

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