Towards the Synthesis of Azoacetylenes

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Dedicated to Prof. *Helmut Schwarz* on the occasion of his 60th birthday

The synthesis of azoacetylenes (=dialkynyldiazenes) **1** and **2** has been investigated. They represent a still elusive class of chromophores with potentially very interesting applications as novel bistable photochemical molecular switches or as antitumor agents (*Fig. 1*). Our synthetic efforts have led us alongside three different approaches (*Scheme 1*). In a first route, it was envisioned to generate the azo (=diazene) bond by photolysis of *N,N′*-dialkynylated 1,3,4-thiadiazolidine-2,5-diones that are themselves challenging targets (*Scheme 2*). Attempts are described to obtain the latter by alkynylation of the parent heterocycle with substituted alkynyliodonium salts. In a conceptually similar approach, the no-less-challenging dialkynylated 9,10-dihydro-9,10-diazanoanthracene (**29**) was to be generated by alkynylation of the unsubstituted hydrazine **28** (*Scheme 6*). In a second route, the generation of the N=N bond from Br-substituted divinylidenehydrazines (ketene-azines) **35** was attempted in a synthetic scheme involving an aza-*Wittig* reaction between azinobis(phosphorane) **36** and (triisopropylsilyl)ketene **37** (*Scheme 7*). Finally, a third approach, based on the formation of the central azo bond as the key step, was explored. This route involved the extrapolation of a newly discovered condensation reaction of *N,N*-disilylated anilines with nitroso compounds (*Scheme 11*, and *Tables 1* and *2*) to the transformation of *N,N*-disilylated ynamine **55** and nitroso-alkyne **54** (*Scheme 13*).

1. Introduction. – (*Z*)- and (*E*)-azoacetylenes (=dialkynyldiazenes) **1** and **2**, respectively (*Fig. 1*), represent an elusive class of chromophores with the potential for a variety of fascinating applications. Similar to azobenzenes (=diphenyldiazenes; **3**/**4**), they could be introduced as photoswitches [1] into a variety of molecular devices, such as photoresponsive receptors and sensors [2], conjugated oligomers [3], or dendrimers [4]. It is well-known that azobenzenes are not thermally bistable, since unfavorable steric interactions in the (*Z*)-isomer induce thermal (*Z*) → (*E*) isomerization (*Fig. 1*) [5]. Introduction of the ethynediyl moieties between the aryl rings and the central bond in the (*Z*)- and (*E*)-diarylated azoacetylenes, **5** and **6**, respectively, should eliminate these unfavorable steric interactions, thereby leading to novel, thermally bistable photoswitches. In analogy, we had shown in previous work that a similar chromophoric extension by ethynediyl insertions into (*Z*)- and (*E*)-stilbenes **7**/**8** [6] provides two-way photoswitchable, thermally bistable (*Z*)- and (*E*)-diarylated 1,2-diethynylethenes (=hex-3-ene-1,5-diynes, DEEs; **9**/**10**) [7] and tetraethynylethenes (=3,4-diethynylhex-3-ene-1,5-diyne, TEEs; **11**/**12**) [8]. Both diarylated DEEs and TEEs feature fully planar, conjugated π-chromophores [9], including the aryl rings, and thermal isomerization is not observed.

Other interesting applications of (*Z*)-azoacetylene (=diethynyldiazene, **1**; R,R′ = H) include its use as precursor in the formation of $C_{12}N_6$ (**13**; *Fig. 2*), the hexaaza analog of

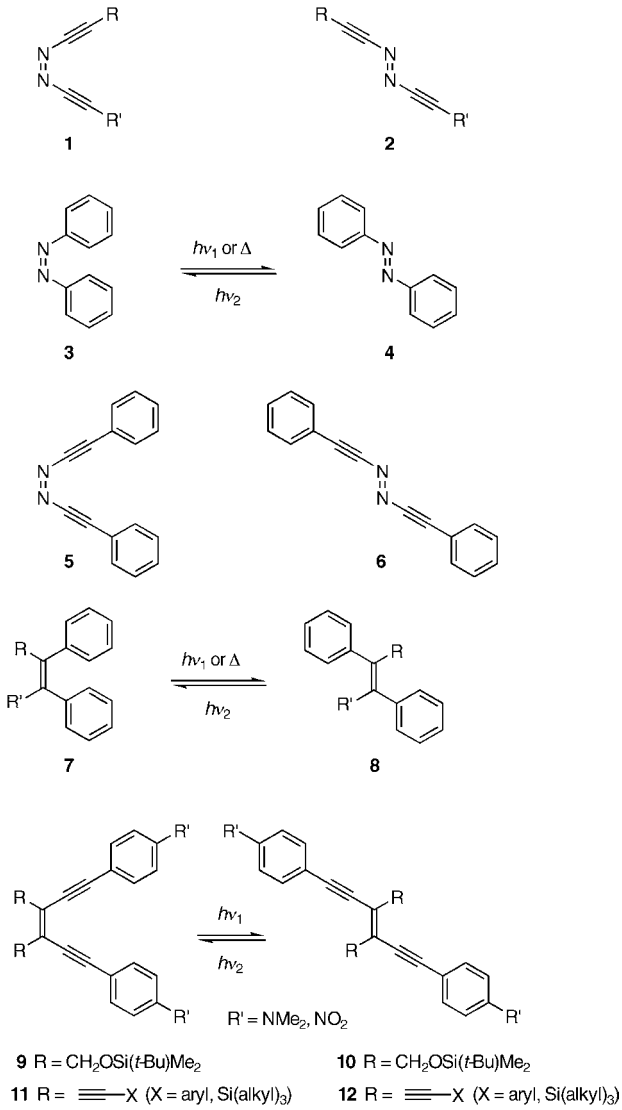


Fig. 1. *Azoacetylenes* **1**, **2**, **5**, **6**, *and their geometric relationship to related classes of photoswitches*

cyclo-C_{18} [10]. Furthermore, (*Z*)-azoacetylenes could find application as novel 'warheads' in anticancer agents, designed after the enediyne antitumor antibiotics [11]. *Bergman* cyclization [12] would provide 3,6-didehydropyrazine biradicals damaging DNA in cancer cells, in analogy to the work by *Chen* and co-workers [13] who showed that (*Z*)-azaenediyne **14** cyclizes to the intermediate 2,5-didehydropyridine biradical (*Fig. 2*) [14].

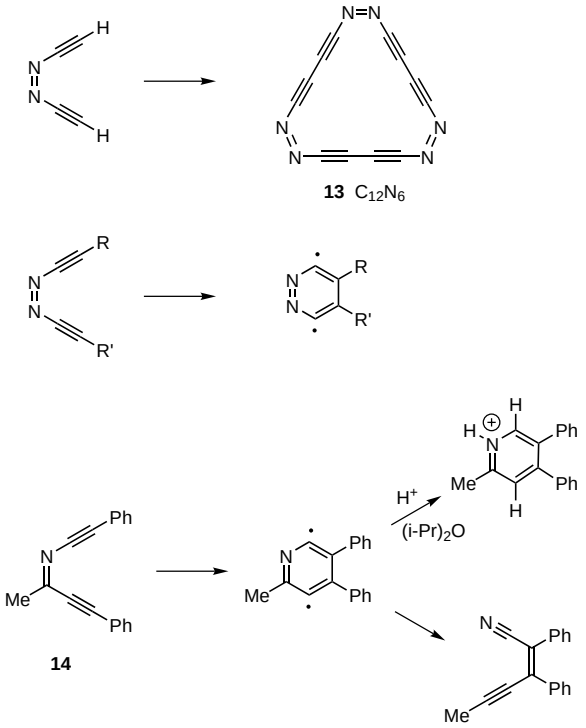
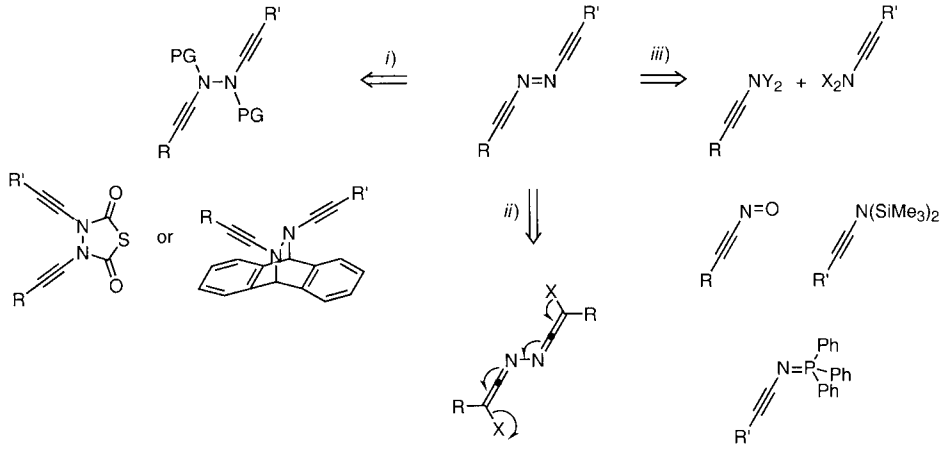


Fig. 2. *Other potential applications of (Z)-azoacetylenes and their analogy to 1-methyl-*N*-(2-phenylethynyl)-propanimine* (**14**)

Despite these fascinating potential applications, no successful or attempted preparation of azoacetylenes **1**/**2** has been described to the best of our knowledge. In fact, their synthesis represents a formidable challenge since the usual routes towards azo derivatives cannot be applied. The coupling of diazonium salts with nucleophiles – although successful in the preparation of (aryl)(arylethynyl)diazenes [15] – would require the intermediate preparation of alkynyldiazonium salts for our purposes. Such intermediates have very low stability and have been shown to undergo nucleophilic attack at the alkynyl C-atom in β-position to the diazonium ion [16]. The condensation of ethynylated amines (ynamines) with nitroso compounds [17], as well as the deprotection/oxidation of *N*,*N*′-dialkynylated hydrazines [18] require protic conditions that are incompatible with the ynamine character of the starting materials. Primary and secondary ynamines tautomerize indeed to the more-stable nitriles and ketenimines, respectively.

Here, we describe a variety of synthetic pathways (*Scheme 1*) explored to prepare various azoacetylenes that, at this stage, remain elusive. Our investigations were focused on three main routes: *i*) the use of protecting groups for 1,2-dialkynylhydrazines that can be removed under nonhydrolytic conditions, followed by oxidation, *ii*) the reductive elimination of dihalogen from bis(2-halogenovinylidene)hydrazines, and *iii*) the formation of the N=N bond through couplings of ynamines and other precursors under aprotic conditions.

Scheme 1. *Synthetic Approaches (i-iii) towards Azoacetylenes Explored in this Investigation.* Some possible precursors are shown.

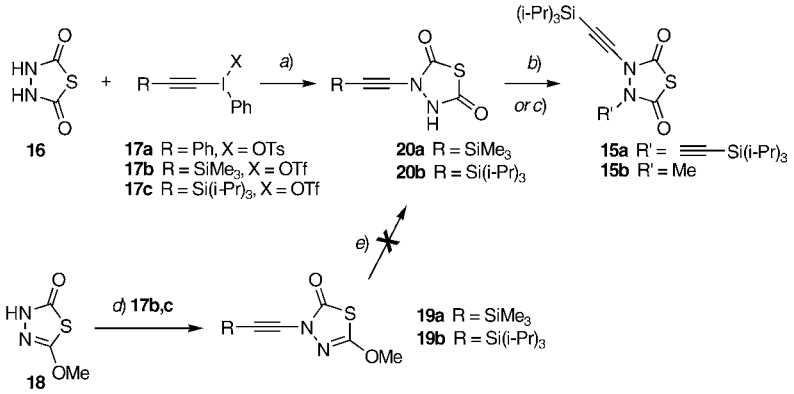


2. Results and Discussion. – 2.1. *Attempted Preparation of Azoacetylenes* via *Protected 1,2-Dialkynylhydrazines.* 2.1.1. *The 1,3,4-Thiadiazolidine-2,5-dione Route.* 1,3,4-Thiadiazolidine-2,5-dione has been shown by *Squillacote et al.* to be a versatile photochemical synthon for the azo group [19]. Starting from *N,N*-disubstituted derivatives, a variety of azo compounds were obtained upon irradiation with UV light (254 nm). Accordingly, the 3,4-dialkynylated 1,3,4-thiadiazolidine-2,5-dione **15a** was selected as our first target (*Scheme 2*). 1,2-Dialkynylated 1,2-diacylhydrazine derivatives, such as **15a**, had not been reported before, making them interesting targets by themselves. To obtain **15a**, it was planned to react the nucleophilic dianion of 1,3,4-thiadiazolidine-2,5-dione (**16**; for the synthesis of **16** and related heterocycles, see [20]) with electrophilic ethynyl species. Alkynyliodonium salts [21] were chosen for this purpose. When their alkyne moiety bears good migrating groups (H, R_3Si, Ph), these salts have been shown to react with a variety of soft nucleophiles, including deprotonated amides, to give the alkynylated derivatives [22].

Attempted reaction of the dianion of **16** with iodonium salts **17a**/**17b** [21] led only to the decomposition of the latter. The use of 5-methoxy-3*H*-1,3,4-thiadiazol-2-one (**18**) as a possible precursor for the stepwise alkynylation allowed isolation of **19a**/**19b** in good yields upon reaction with the alkynyliodonium salts **17b** and **17c**, respectively. Unfortunately, demethylation of **19a**/**19b** under generation of the starting material for the second alkynylation, **20a**/**20b**, failed, with decomposition of the starting material occurring with either Me_3SiI or HI at elevated temperatures. On the other hand, monoalkynylated thiadiazolidinone **20b** could be obtained by alkynylation of **16** with $(i\text{-}Pr)_3Si$-protected alkynyliodonium salt **17c**. It was not very stable, though, and decomposed in all attempts to perform the second alkynylation under formation of the target **15a**. In contrast, it was possible to prepare the more-stable *N*-methylated **15b** by quenching deprotonated **20b** with MeI.

The alkynylation of other 1,2-diacylated hydrazines was subsequently investigated. The anion obtained with LHMDS from commercially available dimethyl hydrazodi-

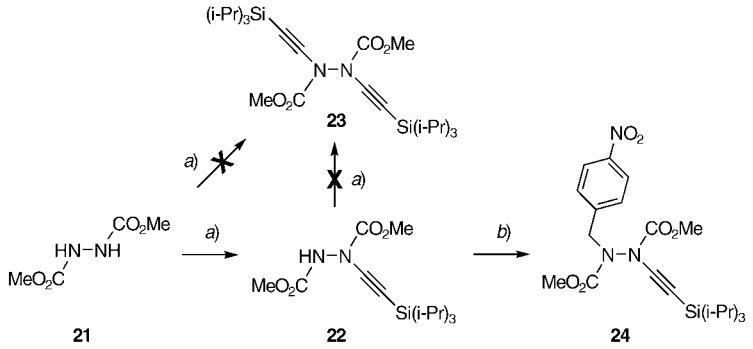
Scheme 2. *Alkynylation of 1,3,4-Thiadiazolidine-2,5-dione* (**16**)



a) LHMDS, THF, $-70° \rightarrow 20°$, 12 h; 0% (**20a**); 79% (**20b**). *b*) **17c**, LHMDS, THF, $-70° \rightarrow 20°$, 12 h; 0%; or KH, DMF, $0° \rightarrow 20°$, 12 h; 0%. *c*) KH, DMF, then MeI (10 equiv.), 20°, 7 h; 48%. *d*) LHMDS, PhMe, $0° \rightarrow 20°$, 12 h; 59% (**19a**); $0° \rightarrow 110°$, 1 h; 58% (**19b**). *e*) Me_3SiI, MeCN; 80°, 12 h; or aq. HI, $20° \rightarrow 100°$, 1 h; 0%. LHMDS = lithium hexamethyldisilazane, TfO = (trifluoromethyl)sulfonyloxy.

carboxylate (**21**) reacted with iodonium salt **17c** to provide mono-alkynylated **22** in 39% yield (*Scheme 3*). However, all attempts to introduce the second alkynyl residue under formation of **23** failed again. In a control reaction, alkylation of **22** with 4-nitrobenzyl bromide gave only 19% of **24**, probably due to the low stability of the starting material.

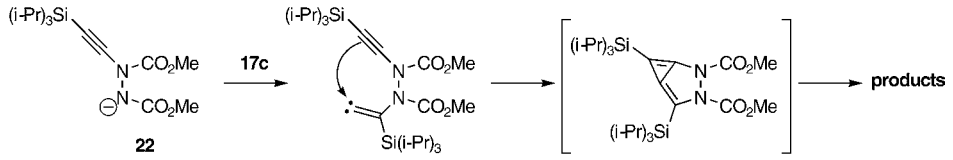
Scheme 3. *Alkynylation of Dimethyl Hydrazodicarboxylate* (**21**)



a) LHMDS, **17c**, PhMe, $0° \rightarrow 20°$, 12 h; 39% (**22**). *b*) KH, DMF, 4-NO_2BnBr, 20°, 12 h; 19%. Bn = benzyl.

The second alkynylation of the heterocycle **20b** (*Scheme 2*) and dimethyl hydrazodicarboxylate **22** (*Scheme 3*) could be thwarted by a side reaction of the intermediate carbenes (*Scheme 4*). It is indeed possible that the intramolecular reaction of the electrophilic carbenes with the ynamide moiety is faster than the desired silyl migration, resulting in the degradation of the starting material. Attempts to

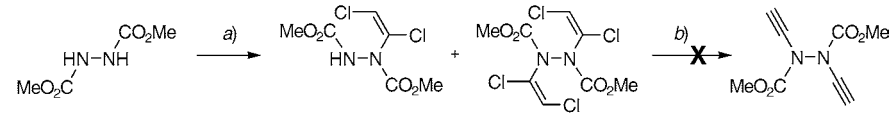
Scheme 4. *A Possible Side Reaction Preventing the Formation of* **23** *from* **22**. A similar mechanism could prevent the dialkynylation of **20b** (*Scheme 2*).



quench the anions with another acetylenic electrophile, namely *tert*-butyl 3-bromoprop-2-ynoate were not successful.

The introduction of the alkynyl fragment was then attempted in a different fashion (*Scheme 5*). Accordingly, **21** was reacted with an excess of ClC≡CCl in the presence of DMAP. This time, it was possible to isolate 1,2-bis(dichlorovinyl)hydrazine derivative **25** in 21% yield, together with rather unstable monovinylated **26** (12%). Attempts to transform **25** into the corresponding dialkynylated hydrazine derivative **27** by reduction with *Rieke*-Zn in THF were unsuccessful. No reaction occurred at room temperature, while heating to reflux led to slow decomposition of the starting material.

Scheme 5. *Dichloroethenylation of Dimethyl Hydrazodicarboxylate* (**22**)



a) ClC≡CCl, DMAP, MeCN/Et_2O, $-40° \rightarrow 20°$, 10 h; 12% (**26**); 21% (**25**). *b*) *Rieke* Zn, THF, $0° \rightarrow 70°$, 12 h; 0%. DMAP = 4-(dimethylamino)pyridine.

In contrast to the ynamides given in *Schemes 2* and *3*, **25** proved to be quite stable, and it was possible to grow crystals suitable for X-ray diffraction (*Fig. 3*,*a*). The dihedral angle C(2)–N(1)–N(6)–C(7) about the hydrazo bond (N–N bond length: 1.39 Å**)** was found to be 63°. The crystal structure revealed a close intermolecular C–H···O contact (d(C···O) = 3.20 Å, angle C–H···O ≈ 157°) between the vinylic C(17)–H moiety and the ester carbonyl O-atom O(3) (*Fig. 3*,*b*). This H-bond should be strengthened by the C–H-acidifying effect of the two Cl-atoms in the vinylic moiety.

2.1.2. *The* retro-Diels–Alder *Route*. In this route, we hoped to dialkynylate the hydrazo moiety in 9,10-dihydro-9,10-diazanoanthracene (**28**) under formation of **29** and to subsequently eliminate anthracene by *retro-Diels–Alder* reaction under formation of the desired azoacetylene (*Scheme 6*). This approach has been used to generate diimide or (*Z*)-azomethane [23] and could potentially be applied to the synthesis of more-elaborate diazenes. The hydrazo compound **28** was obtained by deprotection of the bis-Fmoc derivative **30** (Fmoc = {[(9*H*-fluoren-9-yl)methyl]oxy}-carbonyl) as described in [23c]. It is rather unstable and undergoes *retro-Diels–Alder* reaction in solution within 5 h at room temperature, thereby generating anthracene and diimide [23a]. However, all attempts to react **28** with ClC≡CCl under various conditions failed to give the bis-enamine-type divinyl derivative **31**, a direct precursor of the dialkynylated hydrazine **29**. This result was quite surprising since ClC≡CCl has

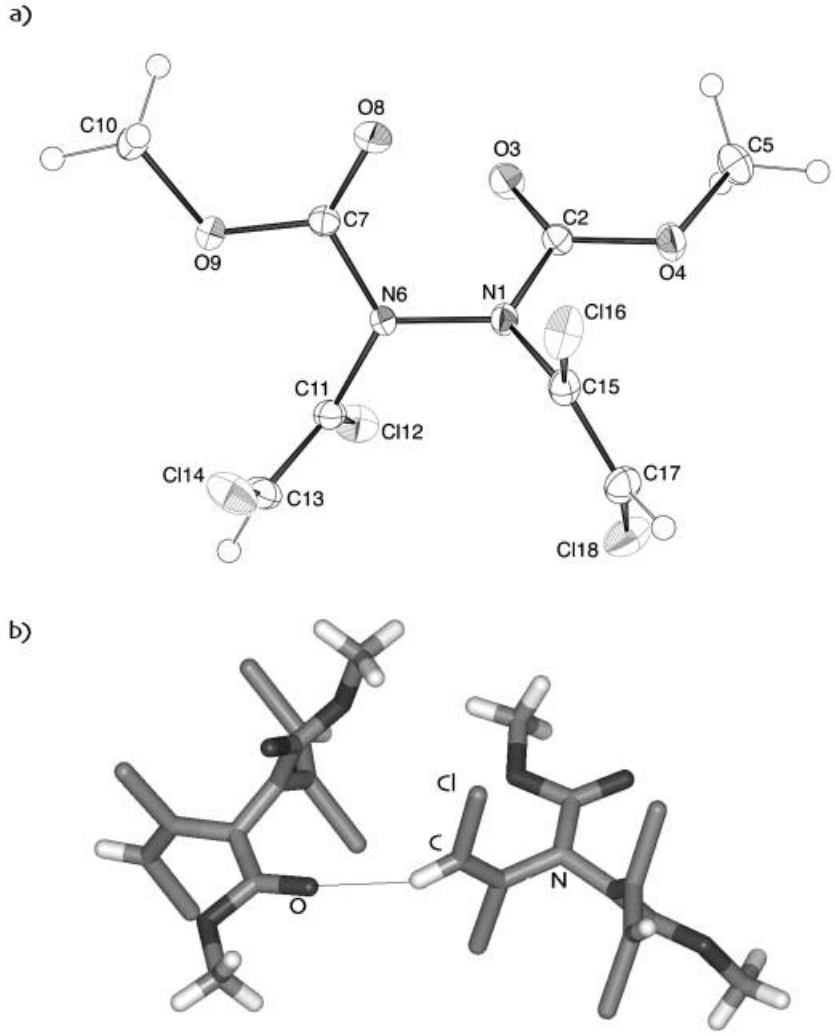
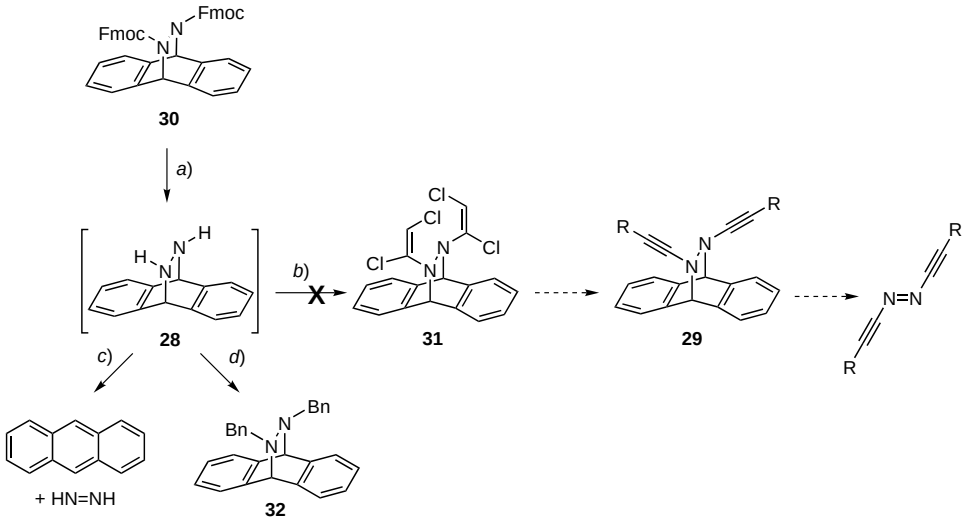


Fig. 3. a) *ORTEP Plot of* **25**. Arbitrary numbering. Atomic displacement parameters obtained at 183 K are drawn at the 50% probability level. Selected bond lengths and bond angles: C(7)–N(6) 1.40, N(6)–C(11) 1.41 C(11)–C(13) 1.32, N(1)–N(6) 1.39, N(1)–C(2) 1.39, N(1)–C(15) 1.41, C(15)–C(17) 1.32 Å; C(7)–N(6)–C(11) 124.6, C(7)–N(6)–N(1) 118.3, C(11)–N(6)–N(1) 116.5, C(2)–N(1)–N(6) 118.2, C(2)–N(1)–C(15) 124.2, C(15)–N(1)–N(6) 116.7°. b) *Crystal structure of* **25** *showing a short intermolecular* $C-H\cdots O$ *H-bond*.

been reported to react with amines under the conditions applied [24]. We surmised that either *i*) the hydrazo group in **28** is too nucleophilic and promotes the polymerization of ClC≡CCl, or *ii*) there is no reaction occurring below the decomposition temperature of one or both of the reactants. A third explanation (*iii*) would be that bis(1,2-dichlorovinyl)diazene is generated in a spontaneous *retro-Diels–Alder* reaction from **31** and decomposes as it is formed. When **28** was reacted with BnBr, which is not more

electrophilic than ClC≡CCl (its alkylation reaction with imidazole requires heating for 2 d in MeCN, while ClC≡CCl undergoes this conversion in less than 12 h at or below room temperature; see [25]), the corresponding bis-adduct **32** was obtained in good yield. This tends to refute hypothesis *ii*. Attempts to react 1,2-dimethylhydrazine with ClC≡CCl only afforded an intractable orange wax, which seems in favor of hypothesis *i*, by which hydrazines promote the polymerization of ClC≡CCl. On the other hand, hypothesis *iii* cannot be ruled out, since large amounts of anthracene were recovered as well, pointing to a *retro-Diels–Alder* reaction. It is, however, difficult to say whether this reaction occurred starting from **28** or from **31**.

Scheme 6. *Exploration of the* retro-Diels–Alder *Route to Azoacetylenes*

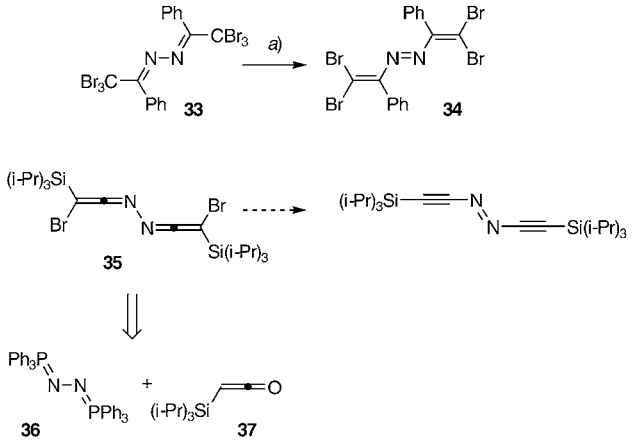


a) Et_2NH, $MeCN/CH_2Cl_2$, 0°, 30 min; 35%. *b*) ClC≡CCl, DMAP, −20°, 24 h; 0%. *c*) $CDCl_3$, 20°, 5 h; 100%. *d*) MeCN, BnBr (4 equiv.), 0° → 20°, 12 h; 72% (20% from **30**).

2.2. *The 1,2-Bis(2-halogenovinylidene)hydrazine Route.* In 1975, *Malament* and *Levi* reported the debromination of azine **33** [26]. In the presence of cyclohexene, diazene **34** was obtained together with 1,2-dibromocyclohexane and 3-bromocyclohexene (*Scheme 7*). We intended to apply this concept to 1,2-divinylidenehydrazine **35**, leading to our target azoacetylene. This divinylidenehydrazine could possibly be obtained in a *Wittig*-type reaction between azinobis(phosphorane) **36** [27] and (triisopropylsilyl)ketene **37**, followed by a bromination–dehydrobromination sequence.

(Triisopropylsilyl)ketene **37** was synthesized by the well-known *retro*-ene reaction of (*tert*-butoxy)alkyne **38** [28], which itself was prepared by known procedures [29]. The synthesis of a bromoketenimine from **37** was then attempted (*Scheme 8*). Bromoketenimines are indeed not very widespread; only five have been reported [30], none of which bears a silyl group. In our approach, reaction of ketene **37** with $Ph_3P{=}NPh$ provided the corresponding ketenimine **39** in good yield (NMR). This ketenimine, however, is somewhat sensitive to heat, and distillation reduced the yield of

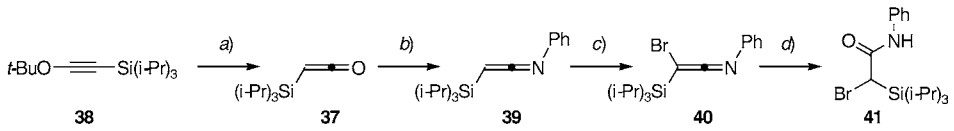
Scheme 7. *Debromination of Azine* **33** *and Proposed Synthesis of an Azoacetylene* via *Divinylidenehydrazine* **35**



a) Cyclohexene, MeOH, AcOEt, Δ, 10 min; 70%. Δ = heating to reflux.

isolated material to 45%. Sequential bromination (Br_2)–dehydrobromination (NEt_3) of **39** afforded the desired bromoketenimine **40** with good conversion. This compound was stable only in solution and decomposed rapidly to a black oil when stored in pure form at room temperature. It was, therefore, converted, by acidic hydrolysis, to α-bromoacetamide **41** that was fully characterized.

Scheme 8. *Synthesis of Bromoketenimine* **40**

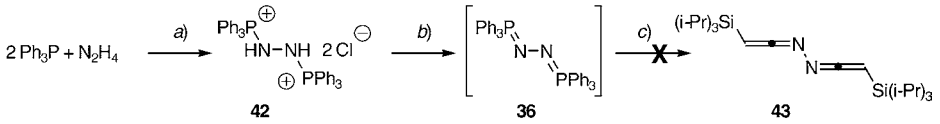


a) 80°, 1 h; 84%. *b*) $Ph_3P{=}NPh$, CH_2Cl_2, 20°, 4 h; 45%. *c*) Br_2, CH_2Cl_2, 20°, then Et_3N (3 equiv.), 20°, 1 h; 65%. *d*) THF, 1N HCl; 20°, 3 h; 37%.

The synthesis of the desired 1,2-divinylidenehydrazine **35** was then explored. For this purpose, the known hydrazobis(triphenylphosphonium) dichloride **42** [27] was reacted with ketene **37** in the presence of a base (*Scheme 9*). Immediate conversion of the starting ketene was observed, but no 1,2-divinylidenehydrazine could be detected in the formed mixture. There was indeed no sign of the characteristic C=N stretching band around 2000 cm^{-1} in the IR spectrum. Unfortunately, it was not possible to assign structures to the compounds in the complex mixture formed.

It is well possible that 1,2-divinylidenehydrazine **43** is unstable. To the best of our knowledge, there are only two reported 1,2-divinylidenehydrazines (**44** and **45**; *Fig. 4*), both of them bearing two electron-withdrawing groups [31]. While **44** seems to be stable, **45** exists in an equilibrium together with two phenoxide radicals resulting from N–N bond cleavage. There are not many other 1,2-vinylidenehydrazines (ketene-hydrazones) reported in the literature. *Schweng* and *Zbiral* reported the easy cleavage of the N–N bond of some 1,2-vinylidenehydrazines, preventing their full character-

Scheme 9. *Attempted Synthesis of* **43**



a) CCl_4, THF, 40°, 4 h; 74%. *b*) Et_3N (5 equiv.), CH_2Cl_2, 20°, 15 min, then *c*) **37** (2 equiv.), CH_2Cl_2, 0° → 20°, 2 h.

ization [32]. Only a perfluorinated 1,2-vinylidenehydrazine reported by *Coe et al.* seems stable [33], pointing again towards a favorable stabilizing effect of electron-withdrawing substituents on the N–N bond. In consequence, future efforts on this route towards azoacetylenes should focus on the coupling of azinobis(phosphorane) **36** with ketenes bearing electron-withdrawing substituents.

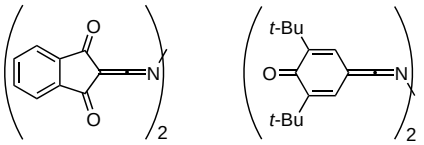
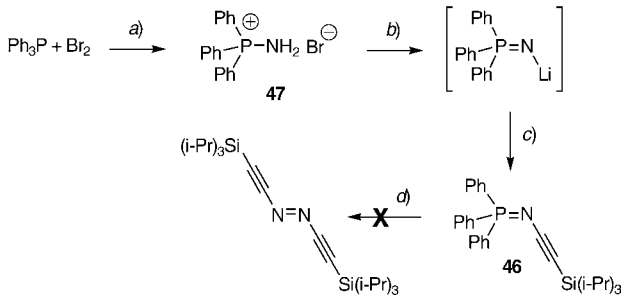


Fig. 4. *Known divinylidenehydrazines* **44** *and* **45** [31]

2.3. *The N=N Connective Approach.* 2.3.1. *The Photocoupling Route.* In 1978, *Yim et al.* reported the irradiation of (arylimino)(triphenyl)phosphoranes ($Ph_3P{=}NAr$) to form the corresponding diarylated azo derivatives in excellent yield [34]. Accordingly, we sought to perform the same reaction with (alkynylimino)(triphenyl)phosphorane **46** (*Scheme 10*).

Scheme 10. *Attempted Photocoupling of* **46**



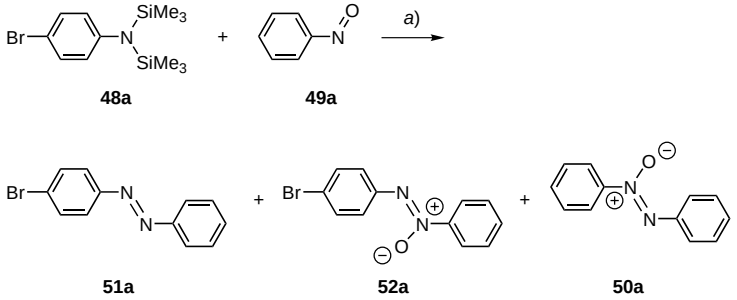
a) MeCN, 10°, 30 min, then NH_3, 20°, 12 h; 89%. *b*) BuLi, THF, −78°, 15 min. *c*) **17c**, −78° → 20°, 1 h; 22% (crude). *d*) PhMe, hν, 12 h; 0%.

Compound **46** was obtained by alkynylation of the aminophosphonium salt **47** with alkynyliodonium salt **17c**. This reaction was not very efficient but the formation of the desired (alkynylimino)(triphenyl)phosphorane could be observed in *ca.* 22% yield in the crude mixture. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra pointed indeed toward the formation of **46** (see *Exper. Part*). This compound is, however, extremely sensitive to

H_2O and could not be isolated in sufficiently pure form for proper characterization. Attempts to perform the photocoupling reaction (medium-pressure Hg lamp, 125 W) on the crude product mixture were not successful; no evidence for the formation of any azo compound or for any change in the composition of the mixture was obtained. On the other hand, the findings of *Yim et al.* were readily reproduced. Therefore, the observed lack of reactivity of crude **46** could be a consequence of light absorption mainly by the impurities in the crude product mixture. Hence, this approach should be re-examined when a better synthesis of **46** has been devised.

2.3.2. *Development of a New Condensation Method towards Azo Compounds.* Since no acidic functionalities can be present in the N=N bond-forming reaction needed for the synthesis of azoacetylenes, we sought to devise a new route towards azo compounds, starting from nonprotic amines. Two research teams had previously reported the synthesis of diazonium salts by the condensation of nitrosyl chloride with either imino(triphenyl)phosphoranes ($Ph_3P{=}NR$) [35a] or *N*,*N*-bis(trimethylsilyl)aniline [35b] (for an application to the synthesis of phenylethynyl diazonium salts, see [35c]). It was thus decided to investigate the coupling of *N*,*N*-disilylated anilines with nitrosobenzene (*Scheme 11* and *Table 1*).

Scheme 11. *Coupling Reaction of* N,N-*Bis(trimethylsilyl)aniline* **48a** *with Nitrosobenzene* **49a**



a) See *Table 1*.

Table 1. *Coupling Attempts between* N,N-*Bis(trimethysilyl)aniline* **48a** *and Nitrosobenzene* (**49a**)

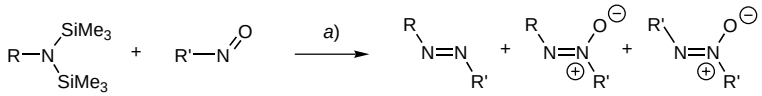
Entry	Reaction conditions	Results
1	CH_2Cl_2, 20°, 24 h	No reaction
2	CH_2Cl_2, $Me_3SiOSO_2CF_3$ (1 equiv.), 0° → 20°, 2 h	Starting material destroyed
3	CH_2Cl_2, $Me_3SiN(SO_2CF_3)_2$ (1 equiv.), −70° → 20°, 3 h	**50a**: 28%
4	DMF, CsF, 20°, 12 h	No reaction
5	THF, Bu_4NF on SiO_2 (0.05 equiv.), −70° → 20°, 12 h	**51a**: 6%; **52a**: 21%; **50a**: 10%
6	THF, MeOK (1 equiv.), 0° → 20°, 12 h	**51a**: 20%; **50a**: 58%

While attempts to couple (triphenyl)(phenylimino)phosphorane ($Ph_3P{=}NPh$) with nitrosobenzene in the presence of various *Lewis* acids ($TiCl_4$, $BF_3 \cdot OEt_2$, $SnCl_4$) led only to the decomposition of starting material, the conversion of the disilylated anilines was more successful. At first, the transformation of **48a** with nitrosobenzene (**49a**) in the presence of $Me_3SiN(CF_3SO_2)_2$ (*Table 1*, *Entry 3*) yielded only the azoxybenzene derivative **50a**, resulting probably from the deoxygenation of nitrosobenzene dimer

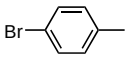
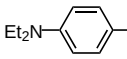
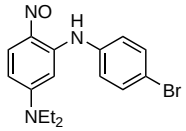
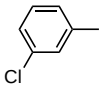
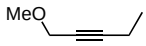
(the deoxygenation of nitrosobenzene dimer has already been reported, albeit in the presence of reducing agents; see [36]). Instead of *Lewis* acid catalysts, *Lewis* bases were evaluated as reaction promoters (*Table 1*, *Entries 5* and *6*). Indeed, in the presence of F^- or MeO^- anions, the desired azobenzene derivative **51a** could be obtained together with the corresponding azoxy derivative **52a** and azoxybenzene **50a** resulting from the homo-coupling of two nitrosobenzene molecules. The MeO^--mediated formation of azobenzene **51a** probably starts by monodesilylation of the disilylated aniline, which then adds to nitrosobenzene, followed by elimination of trimethylsilyloxide (step *i* in *Scheme 12*). The latter can promote the desilylation of another disilylated aniline, generating bis(trimethylsilyl)ether in a catalytic process.

The scope of this new reaction was then briefly investigated (*Table 2*) and shown to be limited to aromatic silylamines. Aliphatic silylamine **48c** promoted only the self-coupling of the nitroso derivatives **49a** and **49c**, leading to symmetric azoxybenzenes **50a**/**50c**, respectively. It must be noted that no such homo-coupling of the nitroso components occurs in the absence of silylamine! The reaction between **48a** and **49c** also afforded a small amount (6%) of nitrosoaniline **53** resulting from nucleophilic aromatic substitution.

Table 2. *Reaction of* N,N-*Disilyl Amines* **48a**–**48c** *and Nitroso Compounds* **49a**–**49c** *in the Presence of MeOK.* Reaction conditions: *a*) MeOK, THF, 0° → 20°, 12 h.



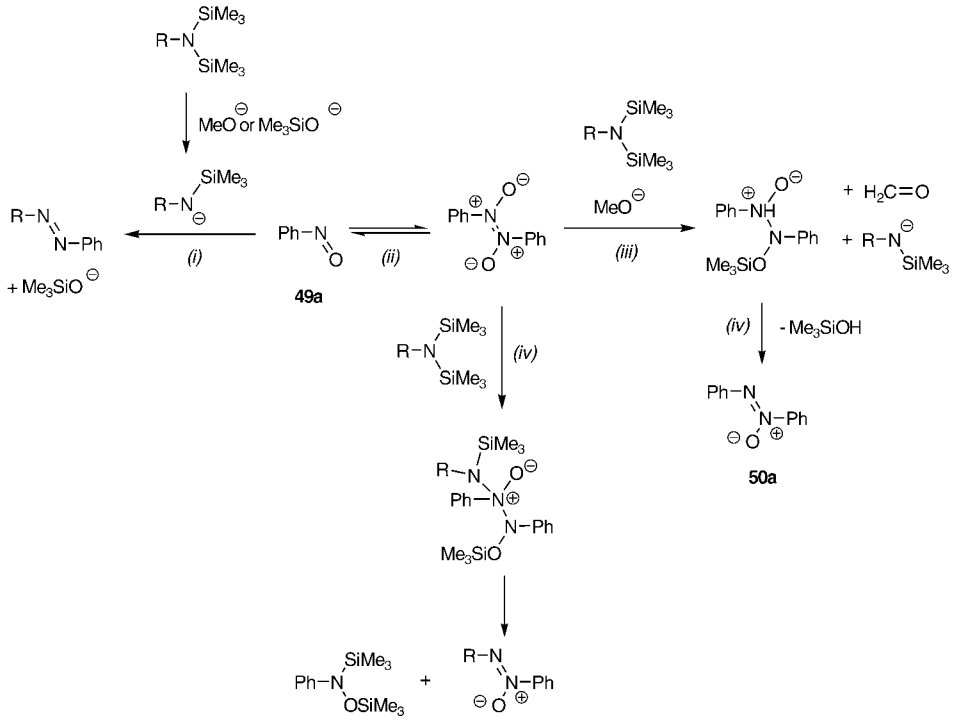
48 **49** **51** **52** **50**

R	R′	Yields		
 (**48a**)	Ph (**49a**)	**51a**: 20%	0	**50a**: 58%
48a	*t*-Bu (**49b**)	**51b**: 61% [a])	0	0
48a	 (**49c**)	 (**53**): 6%	**52c**: 16%	**50c**: 33%
 (**48b**)	**49a**	**51d**: 12% [a])	**52d**: 16% [a])	**50a**: 16% [a])
 (**48c**)	**49a**	0	0	**50a**: 70%
48c	**49c**	0	0	**50c**: 61%

[a]) Obtained with Bu_4NF on SiO_2 (0.5 equiv.).

Our results are tentatively explained by competition between the addition of mono-desilylated aniline to nitrosobenzene (**49a**) (step *i*) and the silyl-amine-promoted reduction of nitrosobenzene or its dimer [37] by the MeO^- ion (step *ii*, *Scheme 12*). Although it has never been reported that nitrosobenzene is reduced by alkoxides, it is the case for nitrobenzene [38]. The disilyl amine somehow accelerates this reduction (steps *iii* and *iv*), since no reaction occurs without it; it possibly assists as an electron shuttle in one-electron transfer reduction steps. In the case of alkylamine **48c** (*Table 2*), the desilylation is probably slower compared to the aromatic amine due to the higher N-basicity. Hence, the heterocoupling reaction (step *i*) may become too slow to be competitive with the reduction of nitrosobenzene or its dimer, and is no longer observed. Another reduction mechanism must be at play in the case of the F^--catalyzed reaction.

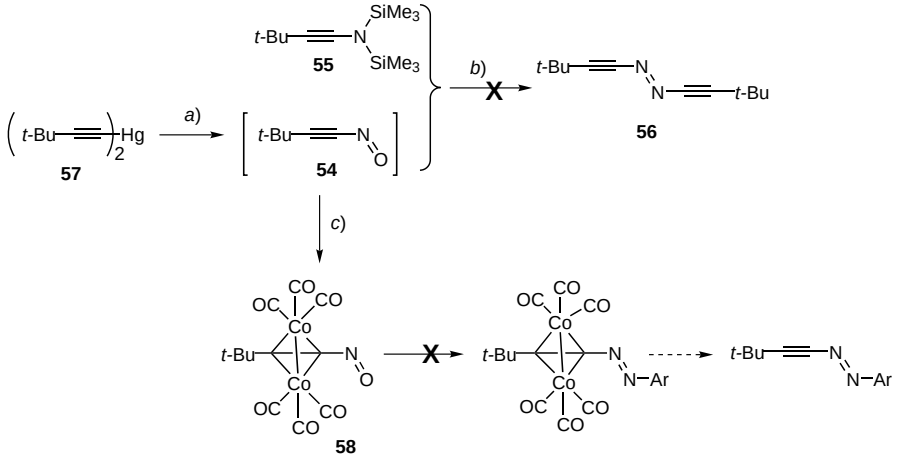
Scheme 12. *Possible Mechanism for the Formation of Hetero- and Homo-Coupled Products in the MeO^--Mediated Conversion of Disilylated Anilines with Nitrosobenzene*



2.3.3. *Application of the New N=N Bond-Forming Reaction to Acetylenic Derivatives.* Although the yields of the new coupling reaction (*Sect. 2.3.2*) are rather modest, the condensation between nitrosoalkyne **54** and *N*,*N*-disilylated ynamine **55** under formation of azoacetylene **56** was explored (*Scheme 13*). *tert*-Bu-Substituted alkynes were chosen in the hope that the steric bulk would impart some stability to starting materials and product. As a result, homo- and heterocoupling would lead to the identical product **56**. The use of silyl protecting groups on the alkynes was not advised,

as they might be cleaved under the desilylating conditions of the reaction. Both alkynes **54** and **55** were obtained according to the literature procedures [39]. It has to be mentioned that nitroso-alkyne **54** cannot be obtained by reacting the lithium salt of 3,3-dimethylbut-1-yne with nitrosyl tetrafluoroborate. The use of the toxic Hg salt **57** is, thus, mandatory. When the coupling reaction was attempted at $-40°$, no conversion was observed, whereas raising the temperature above $-20°$ led to the destruction of the starting nitrosoalkyne. This was not surprising, since **54** is known to decompose at temperatures above $-40°$ [39c].

Scheme 13. *Attempted Coupling between Alkynyl Derivatives* **54** *and* **55**



a) NOCl, CH_2Cl_2, $-70°$, 15 min then *b*) or *c*). *b*) MeOK or Bu_4NF, THF, $-40° \rightarrow 20°$, 3 h; 0%. *c*) $[Co_2(CO)_8]$, CH_2Cl_2, $-70° \rightarrow 20°$, 2 h; 49%.

Accordingly, the nitroso compound **54** was stabilized through its Co complex **58**. The reaction with octacarbonyldicobalt provided a brown solid showing IR absorptions at 2000 and 1450 cm^{-1}, which could be assigned to CO and NO stretching bands, respectively. The ^{1}H-NMR spectrum indicated the presence of the *t*-Bu group. We could, however, not obtain a satisfying mass spectrum nor an elemental analysis of this molecule, as its instability in solution precluded any thorough purification. This compound was nonetheless submitted to the coupling reaction with the *N*,*N*-disilylated aniline **48a**, but no conversion of **48a** to the desired coupled product could be observed. Only desilylated 4-bromoaniline could be recovered. The complex **58** eventually had completely decomposed after an extended reaction time.

3. Conclusions and Outlook. – After this work, the targeted azoacetylenes **1** and **2** remain elusive. Although the alkynylation of amides with alkynyliodonium salts provides a suitable entry into simple *N*-alkynyl amides, this method does not seem appropriate for the construction of dialkynylated hydrazides (*Schemes 2* and *3*), the direct precursors of azoacetylenes. Even though the anions of the monoalkynylated hydrazides **20b** and **22** did not react with *tert*-butyl 3-bromoprop-2-ynoate, the second alkynylation could possibly be achieved in future work by applying the recently

published protocol for Cu-catalyzed hetero-cross-coupling of bromoacetylenes to amides [40]. More indirect approaches to dialkynylated 1,3,4-thiadiazolidine-2,5-diones, such as **15a** – direct precusors to azoacetylenes – remain to be explored. By *N,N*-dialkylation or diacylation of heterocycle **16**, versatile synthons for C≡C moieties, such as aldehydes or diethyl vinyl phosphates, could be introduced and subsequently transformed into the alkynyl residues. Similar indirect routes could also be pursued for the dialkynylation of 9,10-dihydro-9,10-diazanoanthracene (**28**).

Our attempts to synthesize bis(2-bromovinylidene)hydrazine **35** as a precursor to azoacetylenes were also not successful. Although the envisioned aza-*Wittig* reaction could be applied to the synthesis of bromo(triisopropylsilyl)ketenimine **40**, the reaction of azinobis(phosphorane) **36** with (triisopropylsilyl)ketene **37** did not afford bis(vinylidene)hydrazine **43**. In view of the low stability of the ketenimine **40**, the synthesis of **35** could prove very difficult.

Although aprotic coupling conditions for the reaction between *N,N*-disilylated anilines and nitroso compounds could be successfully developed (*Tables 1* and *2*), their application to the construction of azoacetylenes requires conditions that allow the coupling partners to react at or below $-40°$, owing to the low stability of the nitrosoacetylene **54** above that temperature. Obtaining azoacetylenes through an N=N bond-forming reaction could possibly be more successful by the light-promoted coupling of *pure* (alkynylimino)phosphorane **46**. However, a better access to these compounds needs first to be developed.

Another approach to the synthesis of azoacetylenes not investigated in this work could be based on the addition of alkynyl cuprates to properly substituted hyponitrites (RO−N=N−OR → R′−C≡C−N=N−C≡C−R′). This approach is related to the synthesis of the parent *cis*-3-azahex-3-ene-1,5-diyne from tosylimines [14a]. Sulfonylated hyponitrites are not reported but the acyl derivatives show very low stability at room temperature, undergoing radical N−O bond cleavage [41]. On the other hand, most dialkyl hyponitrites are stable at room temperature [42]; therefore, the success of this approach would require to find a leaving group showing enough stability and, at the same time, sufficient nucleofuge character to react with alkynyl cuprates. It is clear that many routes towards azoacetylenes remain to be explored. But, given the fascinating research objectives that can be targeted once these compounds are in hand (see the *Introduction*), all these efforts seem to be most worthwhile.

Experimental Part

General. Reagents and solvents (reagent-grade) were used without further purification unless otherwise stated. THF and Et_2O were freshly distilled from sodium benzophenone ketyl, and CH_2Cl_2 was freshly distilled from CaH_2. Anh. DMF, stored over molecular sieves, was purchased from *Fluka*. $(i\text{-}Pr)_2NH$ and Et_3N were distilled over CaH_2, and used immediately after distillation. All reactions were performed in oven-dried or flame-dried glassware under an inert atmosphere (N_2 or Ar) unless otherwise stated. Evaporation and concentration *in vacuo* were performed at 35°. Further drying of new compounds was carried out at *ca*. 0.1 Torr. Column chromatography (CC) refers to flash chromatography on SiO_2 *60* (0.02 ± 0.063 mm) from *Fluka*; head pressure of *ca*. 0.3 bar. TLC: *Polygram SIL G/UV$_{254}$* SiO_2-coated plates from *Macherey-Nagel*; visualization by UV light (254 nm) or by coloring with a permanganate or phosphomolybdate soln. M.p.: *Büchi B-540* melting-point apparatus; uncorrected. IR Spectra [cm^{-1}]: *Perkin-Elmer 1600 FT-IR* spectrometer. NMR Spectra (^1H, ^{13}C; δ [ppm], J [Hz]: *Varian Gemini 200*, *Varian Mercury 300*, or *Varian Gemini 300* spectrometer at 298 K with residual solvent peaks as internal reference. EI-MS: *VG-Tribrid* instrument operating at 70 eV. ESI-MS:

Finnigan Mat TSQ 7000 instrument. MALDI-MS: *IonSpec Ultra* instrument, with 2,5-dihydroxybenzoic acid (DHB) or 2,4,5-trihydroxyacetophenone/diammonium citrate 2:1 (THA) as a matrix. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie at ETH Zürich.

X-Ray Crystal Structure of **25**. Crystals were grown by slow evaporation of a soln. of **25** in PhMe. Crystal data at 183 K for $C_8H_8N_2O_4Cl_4$ (M_r 337.96): monoclinic space group $P2(1)/n$, $D_c = 1.673$ g/cm^3, $Z = 4$, $a = 7.7520(2)$, $b = 13.1318(3)$, $c = 13.6012(3)$ Å, $\alpha = 90.00$, $\beta = 104.241(1)$, $\gamma = 90.00°$, $V = 1342.02(5)$ Å^3. *Bruker-Nonius Kappa-CCD*, MoK_α radiation, $\lambda = 0.7107$ Å. The structure was solved by direct methods [43] and refined by full-matrix least-squares analysis [44] including an isotropic extinction correction. All heavy atoms were refined anisotropically (H-atoms isotropic, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.030$, $wR(F^2) = 0.0911$ for 172 parameters and 2798 reflections with $I > 2\sigma(I)$ and $\theta < 27.48°$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre*, deposition No. CCDC 208636. Copy of the data can be obtained free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

3-Methyl-4-[(triisopropylsilyl)ethynyl]-1,3,4-thiadiazolidine-2,5-dione (**15b**). A soln. of **20b** (100 mg, 335 μmol) in DMF (2 ml) was added to a suspension of KH (74 mg, 368 μmol) in DMF (2 ml). After stirring for 15 min at 20°, MeI (208 μl, 475 mg, 3.35 mmol) was added to the mixture. After stirring for 7 h at 20°, the mixture was diluted with CH_2Cl_2 (30 ml) and extracted with H_2O (2 × 20 ml). The org. phase was dried ($MgSO_4$) and concentrated *in vacuo*. The residue (130 mg of a yellow oil) was purified (CC; CH_2Cl_2) to yield **15b** (50 mg, 48%). A total of 40 mg (40%) of starting material was also recovered. Colorless oil. IR (neat): 1128*m*, 1292*m*, 1691*s*, 1732*s*, 2171*s*, 2865 s, 2943*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.11 (*m*, 21 H); 3.47 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 11.2; 18.6; 31.9; 81.7; 85.7; 161.1; 170.6. EI-MS: 312 (M^+). HR-EI-MS: 269.0770 ([M – (i-Pr)]$^+$, $C_{11}H_{17}N_2O_2SSi^+$; calc. 269.0780).

*5-Methoxy-3*H*-1,3,4-thiadiazol-2-one* (**18**). A suspension of hydrazinecarbothioic acid *O*-methyl ester (1.0 g, 9.42 mmol) in CH_2Cl_2 (20 ml) was cooled to 0°, and a soln. of triphosgene (1.0 g, 3.30 mmol) in CH_2Cl_2 (20 ml) was slowly added so that the temp. was kept below 10°. The mixture was stirred for 30 min at 20°, then sat. aq. $NaHCO_3$ soln. (20 ml) was added, and stirring was continued for 15 min. The mixture was filtered, and the solid was washed with CH_2Cl_2. The phases were separated, and the aq. phase was washed with CH_2Cl_2 (3 × 20 ml). The combined org. phases were dried ($MgSO_4$) and concentrated *in vacuo*. The residual solid was recrystallized from MeOH/H_2O 1:1 to give **18** (1.1 g, 88%). White solid. M.p. (dec.) 136–137° ([20a]: 135°). IR (CH_2Cl_2): 1269*s*, 1421*s*, 1591*s*, 1706*s*, 2305*s*, 2986*s*, 3413*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.98 (*s*, 3 H); 9.00 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 57.3; 159.9; 170.1.

*5-Methoxy-3-[(trimethylsilyl)ethynyl]-3*H*-1,3,4-thiadiazol-2-one* (**19a**). To HMDS (0.89 ml, 4.23 mmol) in PhMe (8 ml) at 0°, BuLi (2.63 ml of a 1.6M soln. in hexane, 4.21 mmol) was slowly added, and the mixture was stirred at 0° for 15 min. A soln. of **18** (490 mg, 3.71 mmol) in PhMe (32 ml) was added, and the mixture was stirred for 20 min at 0°. Finally, **17b** (2.0 g, 4.44 mmol) was added in portions, and the mixture was stirred overnight at 20°. After filtration through a plug of SiO_2, the precipitate was washed with PhMe (500 ml). The combined filtrates were concentrated *in vacuo* to afford 1 g of an orange solid that was purified (CC; PhMe) to give **19a** (500 mg, 59%). Pale-yellow solid. M.p. 74–75°. IR (CH_2Cl_2): 837*s*, 1265*s*, 1589*s*, 1699*s*, 2247*m*, 2262*m*, 2951*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.24 (*s*, 9 H); 4.04 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): –0.1; 57.8; 78.8; 88.6; 157.4; 167.2. EI-MS: 228 (M^+). HR-EI-MS: 213.0149 ([M – Me]$^+$, $C_7H_9N_2O_2SSi^+$; calc. 213.0152).

*5-Methoxy-3-[(triisopropylsilyl)ethynyl]-3*H*-1,3,4-thiadiazol-2-one* (**19b**). To HMDS (0.75 ml, 3.56 mmol) in PhMe (7 ml) at 0°, BuLi (2.22 ml of a 1.6M soln. in hexane, 3.55 mmol) was slowly added, and the mixture was stirred at 0° for 15 min. A soln. of **18** (413 mg, 3.12 mmol) in PhMe (30 ml) was added dropwise, and the resulting mixture was stirred for 20 min at 0°. Finally, **17c** (2.0 g, 3.74 mmol) was added in portions, and the mixture was stirred for 1 h at 110°. After filtration through a plug of SiO_2, the precipitate was washed with PhMe (500 ml), and the combined filtrates were concentrated *in vacuo* to afford 1.34 g of an orange solid, which was purified (CC; PhMe/pentane 1:1) to give **19b** (570 mg, 58%). Pale-yellow solid. M.p. 55–57°. IR (CH_2Cl_2): 1265*s*, 1589*s*, 1695*s*, 2248*m*, 2255*m*, 2965*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.11 (*m*, 21 H); 4.04 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 11.2; 18.6; 57.8; 75.5; 90.4; 157.0; 167.4. EI-MS: 312 (M^+). HR-EI-MS: 269.0772 ([M – (i-Pr)]$^+$, $C_{11}H_{17}N_2O_2SSi^+$; calc. 269.0780).

3-[(Triisopropylsilyl)ethynyl]-1,3,4-thiadiazolidin-2,5-dione (**20b**). *Method A.* BuLi (1.16 ml of a 1.6M soln. in hexane, 1.86 mmol) was added dropwise at 0° to a stirred soln. of HMDS (393 μl, 301 mg, 1.86 mmol) in THF (9 ml). After stirring for 15 min, **16** (100 mg, 847 μmol) in THF (18 ml) was added dropwise. After 30 min, the cloudy mixture was cooled to –70°, and **17c** (905 mg, 1.69 mmol) in THF (9 ml) was slowly added. After warming to 20°, stirring was continued for 12 h. The mixture was poured into sat. aq. NH_4Cl soln. (20 ml) and

extracted with Et_2O (3×20 ml). The org. phases were dried ($MgSO_4$) and concentrated *in vacuo* to yield 450 mg of a yellow oil, which was purified (CC; MeOH/CH_2Cl_2 $0:1 \rightarrow 1:9$) to provide **20b** (190 mg, 79%). Unstable yellow oil. ^{1}H-NMR (CD_3OD, 300 MHz): 1.10 (*m*, 21 H). ^{13}C-NMR (CD_3OD, 75 MHz): 12.5; 19.0; 73.2; 93.7; 162.5; 172.5.

Method B. To a stirred suspension of KH (374 mg, 1.86 mmol) in THF (9 ml) at 0°, a soln. of **16** (100 mg, 847 μmol) in THF (18 ml) was added dropwise. After 30 min, the mixture was cooled to −78°, and **17c** (905 mg, 1.69 mmol) in THF (9 ml) was slowly added. After warming to 20°, stirring was continued for 24 h. The orange mixture was poured into sat. aq. NH_4Cl soln. (20 ml) and extracted with Et_2O (3×20 ml). The combined org. phases were dried ($MgSO_4$) and concentrated *in vacuo* to yield 450 mg of a yellow oil, which was purified (CC, MeOH/CH_2Cl_2 $0:10 \rightarrow 1:9$) to give **20b** (130 mg, 51%).

Dimethyl 1-[(Triisopropylsilyl)ethynyl]hydrazine-1,2-dicarboxylate (**22**). To HMDS (434 μl, 332 mg, 2.06 mmol) in PhMe (2 ml) at 0°, BuLi (1.29 ml of a 1.6M soln. in hexane, 2.06 mmol) was slowly added, and the mixture was stirred at this temp. for 15 min. A soln. of **21** (138 mg, 936 μmol) in PhMe (8 ml) and THF (5 ml) was added dropwise, and the mixture was stirred for 20 min at 0°. Finally, **17c** (1.0 g, 1.87 mmol) was added portionwise, and stirring was continued for 12 h at 20°. The yellow mixture was poured into sat. aq. NH_4Cl soln. (30 ml) and extracted with Et_2O (3×20 ml). The combined org. phases were dried ($MgSO_4$) and concentrated *in vacuo* to yield 500 mg of a yellow oil, which was purified (CC, AcOEt/PhMe $0:1 \rightarrow 1:9$) to provide **22** (120 mg, 39%). Unstable colorless oil. IR (neat): 1068*s*, 1213*s*, 1457*s*, 1517*s*, 1734*s*, 2182*s*, 2929*s*, 3308*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.06 (*s*, 21 H); 3.78 (*s*, 3 H); 3.85 (*s*, 3 H); 7.10 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 11.3; 18.5; 53.4; 54.8; 71.1; 94.6; 154.4; 155.0. EI-MS: 110 (100), 124 (60), 180 (99), 285 (37), 328 (0.5, M^+).

Dimethyl 1-(4-Nitrobenzyl)-2-[(triisopropylsilyl)ethynyl]hydrazine-1,2-dicarboxylate (**24**). A soln. of **22** (110 mg, 335 μmol) in DMF (2 ml) was added to a suspension of KH (80 mg, 402 μmol) in DMF (2 ml), and the mixture was stirred at 20° for 30 min. 4-Nitrobenzyl bromide (145 mg, 670 μmol) was then added, and the mixture was stirred for 12 h. The mixture was poured into H_2O (20 ml) and extracted with CH_2Cl_2 (3×20 ml). The combined org. phases were dried ($MgSO_4$), concentrated *in vacuo*, and purified (CC, PhMe/AcOEt $1:0 \rightarrow 98:2$) to yield **24** (30 mg, 19%). Pale-yellow oil. IR (neat): 1348*s*, 1441*s*, 1524*s*, 1608*w*, 1755*s*, 2179*m*, 2865*m*, 2945*m*, 3031*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.06 (*s*, 21 H); 3.82 (*s*, 6 H); 4.61 (*d*, $J = 15.0$, 1 H); 5.04 (br. *d*, $J = 15.0$, 1 H); 7.57 (*d*, $J = 8.7$, 2 H); 8.15–8.18 (*d*, $J = 8.7$, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 11.0; 18.4; 52.6; 54.2; 54.8; 77.2; 93.5; 123.6; 129.4; 142.8; 147.6; 153.7; 155.0. HR-MALDI-MS: 486.2036 ($[M + Na]^+$, $C_{22}H_{33}N_3NaOSi^+$; calc. 486.2036).

*Dimethyl 1,2-Bis[(*E*)-1,2-dichloroethenyl]hydrazine-1,2-dicarboxylate* (**25**) *and Dimethyl 1-[(*E*)-1,2-Dichloroethenyl)hydrazine-1,2-dicarboxylate* (**26**). A soln. of **21** (200 mg, 1.35 mmol) and DMAP (181 mg, 1.49 mmol) in MeCN (5 ml) was cooled to −40°, and ClC≡CCl (1.35 ml, 4.05 mmol) was slowly added. The mixture was stirred at 20° for 12 h, and then the solvent was evaporated *in vacuo*. The brown oily residue was dissolved in CH_2Cl_2 and washed with H_2O. The org. phase was dried ($MgSO_4$) and concentrated *in vacuo* to yield 0.5 g of a brown oil, which was purified (CC, CH_2Cl_2) to afford **25** (100 mg, 21%). Further elution (CH_2Cl_2/AcOEt 9:1) provided **26** (40 mg, 12%).

Data of **25**: White solid. IR (CH_2Cl_2): 1276*s*, 1333*s*, 1441*s*, 1614*w*, 1754*s*, 2853*w*, 3018*w*, 3092*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.89 (*s*, 6 H); 6.39 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 54.6; 119.4; 128.6; 151.5. EI-MS: 59 (100), 163 (33), 165 (20), 257 (20), 259 (20), 301 (12), 303 (12), 338 (1.5, M^+). Anal. calc. for $C_8H_8N_2O_4Cl_4$ (337.97): C 28.53, H 2.39, N 8.29; found: C 29.02, H 2.45, N 8.05. X-Ray: see *Fig. 3*.

Data of **26:** Unstable, colorless oil. IR (CH_2Cl_2): 1243*s*, 1302*s*, 1442*s*, 1489*m*, 1617*m*, 1746*s*, 2959*m*, 3033*m*, 3400*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.79 (*s*, 3 H); 3.86 (*s*, 3 H); 6.26 (*s*, 1 H); 6.8 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 53.4; 54.6; 116.8; 130.3; 155.7.

11,12-Dibenzyl-9,10-dihydro-9,10-diazanoanthracene (**32**). To a soln. of **30** (991 mg, 1.52 mol) in CH_2Cl_2 (70 ml), MeCN (7 ml) was added. The soln. was cooled to 0°, and Et_2NH (7 ml) was added over a period of 15 min. After stirring at 0° for 25 min, the solvents were evaporated *in vacuo* at 0°. The resulting yellow solid was suspended in Et_2O (8 ml) and re-evaporated to remove any residual Et_2NH. The residual solid was re-dissolved in pre-cooled MeCN (7 ml) at 0°, and BnBr (1.56 g, 9.11 mmol) was added. The mixture was stirred for 3 h at 0° and then for 12 h at 20°. Evaporation *in vacuo* afforded a residue, which was dissolved in CH_2Cl_2 and washed with sat. aq. NH_4Cl soln. The org. phase was dried ($MgSO_4$) and concentrated *in vacuo* to yield 1 g of yellow oil solid, which was purified (CC; PhMe/hexane $0:1 \rightarrow 1:0$) to give **32** (150 mg, 20%). White solid. M.p. 160–162°. IR (CH_2Cl_2): 730*s*, 1255*s*, 1275*s*, 1459*m*, 1468*m*, 2847*m*, 3029*m*, 3053*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.25 (br. *s*, 2 H); 3.50 (br. *s*, 2 H); 4.84 (*s*, 2 H); 7.26 (*m*, 18 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 61.6; 61.8; 124.9; 126.5;

127.1; 128.2; 129.7; 138.5; 140.1. ESI-MS: 389 (100, MH^+). Anal. calc. for $C_{28}H_{24}N_2$ (388.51): C 86.56, H 6.23, N 7.21; found: C 86.51, H 6.35, N 7.05.

(Triisopropylsilyl)ethenone (**37**) [45]. Alkyne **38** (13 g, 51.08 mmol) was heated to 80° for 1 h. After the end of the gas evolution, stirring was continued for 30 min, then the product was distilled at 60°/0.02 Torr to afford pure **37** (8.5 g, 84%). Colorless liquid. B.p. 90–100°/1 Torr. IR (neat): 883*m*, 995*m*, 1106*w*, 1273*w*, 1367*w*, 1462*m*, 1552*s*, 2106*s*, 2866*s*, 2944*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.06 (*m*, 21 H); 1.65 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): −7.3; 12.1; 18.2; 178.9.

*1-(*tert*-Butoxy)-2-(triisopropylsilyl)ethyne* (**38**) [29b]. To a soln. of LDA, prepared from BuLi (69 ml of a 1.6M soln. in hexane, 110.40 mmol) and $(i\text{-Pr})_2NH$ (17.5 ml, 13.51 g, 133.5 mmol) in THF (100 ml) at −60°, (*Z*)-2-bromo-1-(*tert*-butoxy)ethene (8.95 g, 49.98 mmol) in THF (20 ml) was added. The mixture was stirred for 2 h while allowing it to warm to 20°. A dark-red color slowly developed. The mixture was then cooled to −20°, and $(i\text{-Pr})_3SiCl$ (12.81 ml, 11.54 g, 59.88 mmol) was added. After stirring for 4 h at 20°, the mixture was poured into sat. aq. $NaHCO_3$ soln. (100 ml), the org. layer was separated, and the aq. layer was extracted with petroleum ether (3 × 20 ml). The combined org. phases were washed with 0.5N HCl (2 × 100 ml), H_2O (100 ml), and sat. aq. NaCl soln. (150 ml), and dried ($MgSO_4$). Solvent evaporation at 20° afforded crude **38** as a dark red liquid (16 g), which was used directly in the next reaction. The crude product was purified by filtration through a short column (6 g of SiO_2 containing 3% (*v*/*v*) Et_3N) and elution with pentane (250 ml) to give **38** (15 g, 100%). Pale-yellow liquid. IR (CH_2Cl_2): 883*m*, 1148*m*, 1250*w*, 1370*m*, 1462*m*, 1717*m*, 2166*s*, 2864*s*, 2942*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.06 (*s*, 21 H); 1.42 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 11.7; 17.7; 18.8; 26.9; 86.6; 107.5.

N-*[2-(Triisopropylsilyl)ethenylidene]aniline* (**39**). A soln. of **37** (200 mg, 1.01 mmol) in CH_2Cl_2 (5 ml) was added to $Ph_3P{=}NPh$ (356 mg, 1.01 mmol) in CH_2Cl_2 (5 ml), and the mixture was stirred until disappearance of the band at 2100 cm^{-1} in the IR spectrum (*ca.* 4 h). Evaporation *in vacuo* afforded a pale-yellow solid residue, which was taken up in hexane (*ca.* 10 ml). Filtration afforded a filtrate that was concentrated *in vacuo* to give 200 mg of a yellow oil. Distillation under reduced pressure afforded **39** (110 mg, 45%). Colorless liquid. B.p. 100–110°/0.03 Torr. IR (CCl_4): 1119*s*, 1256*s*, 1437*s*, 1483*s*, 1491*s*, 1591*s*, 1943*s*, 2000*s*, 2865*s*, 2890*m*, 3045*w*, 3078*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.06 (*m*, 21 H); 3.21 (*s*, 1 H); 7.24 (*m*, 3 H); 7.33 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 11.8; 18.5; 31.1; 123.4; 126.3; 129.3; 141.5; 181.2. EI-MS: 274 (0.2, M^+), 230 (11), 131 (100), 103 (99), 75 (97), 61 (35), 28 (30). Anal. calc. for $C_{17}H_{27}NSi$ (273.49): C 74.66, H 9.95, N 5.12; found: C 74.67, H 9.87, N 5.06.

N-*[2-Bromo-2-(triisopropylsilyl)ethylidene]aniline* (**40**). A soln. of Br_2 (34 µl, 105 mg, 658 µmol) in CH_2Cl_2 (5 ml) was added dropwise to **39** (180 mg, 658 µmol) in CH_2Cl_2 (5 ml) until a red color persisted. The soln. slowly turned yellow and then orange. IR Monitoring showed the disappearance of the characteristic band at 2000 cm^{-1} band while a weaker band around 1667 cm^{-1} appeared. After cooling with an ice bath, Et_3N (300 µl, 219 mg, 2.17 mmol) was added, and the soln. was stirred at 20° for 1 h. A new band at 1993 cm^{-1} appeared. The mixture was concentrated *in vacuo* and the solid residue was taken up in hexane (15 ml) and filtered. The filtrate was concentrated to afford **40** (150 mg, 65%). This compound could not be sufficiently purified (CC or distillation) to obtain an elemental analysis. It decomposes rapidly when stored neat under Ar at 20°. Yellow liquid. IR (CCl_4): 1465*w*, 1488*w*, 1592*w*, 1993*s*, 2857*m*, 2946*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.12 (*m*, 18 H); 1.20 (*m*, 3 H); 7.35 (*m*, 5 H). EI-MS: 351 (0.5, M^+), 308 (2), 276 (6), 230 (100), 188 (35), 160 (25), 131 (22).

*2-Bromo-*N*-phenyl-2-(triisopropylsilyl)acetamide* (**41**). Crude **40** (150 mg) was dissolved in THF (5 ml) and stirred for 3 h together with 1N HCl (10 ml). The org. phase was dried ($MgSO_4$) and concentrated *in vacuo*. The resulting brown oil was purified (CC; PhMe/hexane 0:1 → 1:0) to afford **41** (150 mg, 37%). White solid. Mp 75–78°. IR (CH_2Cl_2): 1311*m*, 1441*s*, 1524*s*, 1599*m*, 1667*s*, 2808*s*, 2946*s*, 3397*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.14 (*d*, *J* = 7.5, 9 H); 1.19 (*d*, *J* = 7.5, 9 H); 1.44 (*sept.*, *J* = 7.5, 3 H); 4.14 (*s*, 1 H); 7.13 (*m*, 1 H); 7.34 (*m*, 2 H); 7.50 (*m*, 2 H); 8.35 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 11.9; 18.6; 36.4; 119.9; 124.7; 129.1; 137.4; 167.1. EI-MS: 371 (0.56, M^+), 369 (0.41, M^+), 328 (4), 326 (4), 248 (15), 85 (100). Anal. calc. for $C_{17}H_{28}BrNOSi$ (370.40): C 55.13, H 7.62, N 3.78, Br 21.57; found: C 55.07, H 7.79, N 3.82, Br 21.65.

{[(Triisopropylsilyl)ethynyl]imino}triphenylphosphorane (**46**). BuLi (1.16 ml of a 1.6M soln. in hexane, 1.87 mmol) was added dropwise to a suspension of **47** (335 mg, 935 µmol) [46] in THF (12 ml) at −70° under Ar. Stirring was continued for 15 min at this temp., then a soln. of **17c** (500 mg, 935 µmol) in THF (5 ml) was added dropwise. The mixture was stirred for 1 h at −70° and then slowly warmed to 20° (3 h). An NMR analysis of the crude mixture revealed the formation of the desired product, alongside starting material and other products. A quick filtration over SiO_2 (Et_2O) allowed isolation of *ca.* 10 mg (3%) of **46**. Yellow oil. ^{31}P-NMR ($CDCl_3$, 300 MHz): 7.50. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.10 (*m*, 21 H); 7.46 (*m*, 9 H); 7.84 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 11.1; 18.5; 101.0 (*d*, *J* = 150.0); 113.2 (*d*, *J* = 19.0); 128.4 (*d*, *J* = 36.0); 130.6 (*d*, *J* = 11.0); 131.9; 133.0 (*d*, *J* = 120.0).

Reaction between **48a** *and* **49a** *in the Presence of* $Me_3SiN(SO_2CF_3)_2$. A soln. of $HN(SO_2CF_3)_2$ (300 mg, 1.07 mmol) and allyl(trimethyl)silane (186 µl, 134 mg, 1.17 mmol) in CH_2Cl_2 (4 ml) was added dropwise to **49a** (114 mg, 1.07 mmol) in CH_2Cl_2 (5 ml) at $-70°$. The blue soln. turned deep-red, then clear-orange. Aniline **48a** (301 µl, 337 mg, 1.07 mmol) was then added. The mixture was warmed to 20° over 3 h and poured into sat. aq. $NaHCO_3$ soln. The org. phase was dried ($MgSO_4$) and concentrated *in vacuo* to afford 0.3 g of a dark-green solid, which was purified (CC; PhMe/hexane 0:1 → 1:0) to give *azoxybenzene* (**50a**) (30 mg, 28%). Yellow solid. Mp 34–36° (commercial sample: 32–34°). 4-Bromoaniline was recovered as well (50 mg, 27%). Brown solid. M.p. 60–62° (commercial sample: 60–62°).

General Procedures for the Reaction between Bis(trimethylsilyl)amines **48a**–**48c** *and Nitroso Compounds* **49a**–**49c**.

Procedure A. A soln. of amine **48a**–**48c** in THF was added dropwise to a cold (−70°) suspension of nitroso derivative **49a**–**49c** and a catalytic amount of Bu_4NF on SiO_2 in THF (same volume). The mixture was warmed to 20°, stirred for 12 h, and concentrated *in vacuo*. The residue was purified (CC; PhMe/hexane 0:1 → 1:0).

Procedure B. Same as *Procedure A* except that Bu_4NF on SiO_2 was replaced by 1 equiv. of MeOK, and the starting temp. was 0°.

Reaction between **48a** *and* **49a**. According to *Procedure A*, **48a** (263 µl, 295 mg, 934 µmol), **49a** (100 mg, 934 µmol), and Bu_4NF on SiO_2 (42 mg, 47 µmol) in THF (6 ml) gave *1-(4-bromophenyl)-2-phenyldiazene* (**51a**; 15 mg, 6%), *1-(4-bromophenyl)-2-phenyldiazene 2-oxide* (**52a**; 55 mg, 21%), **50a** (95 mg, 58%), and *4-bromoaniline* (90 mg, 56%).

Data of **51a**: Orange solid. M.p. 86–88° ([47]: 88–90°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.51 (*m*, 3 H); 7.65 (*m*, 2 H); 7.80 (*m*, 2 H); 7.92 (*m*, 2 H).

Data of **52a**: Yellow solid. M.p. 72–73° ([48]: 73–74°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.55 (*m*, 5 H); 8.08 (*m*, 2 H); 8.29 (*m*, 2 H).

According to *Procedure B*, **49a** (100 mg, 934 µmol), **48a** (263 µl, 295 mg, 934 µmol), and MeOK (66 mg, 934 µmol) in THF (5 ml) provided **51a** (50 mg, 20%) and **50a** (50 mg, 58%).

Reaction between **48a** *and* **49b**. According to *Procedure A*, **49b** (200 mg, 2.30 mmol), **48a** (726 mg, 2.30 mmol), and Bu_4NF on SiO_2 (210 mg, 230 µmol) in THF (6 ml) gave, after purification (CC; PhMe/hexane 2:8, then AcOEt 100%), *1-(4-bromophenyl)-2-(*tert*-butyl)diazene* (**51b**; 170 mg, 61%) and 4-bromoaniline (10 mg, 30%).

Data of **51b**: Yellow, volatile oil. IR (neat): 830*s*, 1009*s*, 1066*s*, 1362*s*, 1471*s*, 1524*s*, 1579*s*, 1587*s*, 1651*w*, 1905*w*, 2866*m*, 2929*s*, 2971*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.32 (*s*, 9 H); 7.53 (*m*, 2 H); 7.58 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 26.8; 67.9; 123.5; 124.1; 132.0; 151.0. EI-MS: 242 (M^+). HR-EI-MS: 240.0254 (M^+, $C_{10}H_{13}N_2Br^+$; calc. 240.0262).

Reaction between **48a** *and* **49c**. According to *Procedure B*, **49c** (158 mg, 886 µmol), **48a** (250 µl, 280 mg, 886 µmol), and MeOK (62 mg, 886 µmol) in THF (4 ml) yielded, after purification (CC; AcOEt/PhMe/hexane gradient 0:0:1 → 1:0:0), *4-nitroso-3-[(4-bromophenyl)amino]*-N,N-*diethyl-4-nitrosoaniline* (**53**; 20 mg, 6%), *1-(4-bromophenyl)-2-[4-(diethylamino)phenyl]diazene 2-oxide* (**52c**; 50 mg, 16%), *1,2-bis[4-(diethylamino)-phenyl]diazene 1-oxide* (**50c**; 100 mg, 33%) **49c** (40 mg, 25%), and 4-bromoaniline (40 mg, 26%).

Data of **53**: Dark green solid. M.p. 155–157°. IR (CH_2Cl_2): 1140*s*, 1263*s*, 1331*m*, 1492*s*, 1527*m*, 1551*m*, 1620*s*, 2978*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.22 (*t*, *J* = 7.2, 6 H); 3.41 (*q*, *J* = 7.2, 4 H); 5.97 (*d*, *J* = 2.5, 1 H); 6.46 (*dd*, *J* = 9.6, 2.5, 1 H); 7.17 (*d*, *J* = 6.9, 2 H); 7.49 (*d*, *J* = 6.9, 2 H); 8.18 (*d*, *J* = 9.6, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 12.9; 45.3; 88.4; 106.5; 118.2; 125.9; 132.4; 137.3; 138.6; 142.2; 151.5; 154.1. HR-MALDI-MS: 348.0710 (MH^+, $C_{16}H_{19}BrN_3O^+$; calc. 348.0711).

Data of **52c**: Orange solid. M.p. 147–149°. IR (CH_2Cl_2): 822*m*, 1183*m*, 1515*s*, 1598*s*, 2976*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.22 (*t*, *J* = 7.2, 6 H); 3.44 (*q*, *J* = 7.2, 4 H); 6.64 (*d*, *J* = 9.6, 2 H); 7.55 (*d*, *J* = 9.0, 2 H); 7.97 (*d*, *J* = 9.0, 2 H); 8.15 (*d*, *J* = 9.6, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 12.4; 44.6; 110.1; 121.6; 124.0; 126.7; 131.6; 136.4; 143.4; 150.1. HR-MALDI-MS: 348.0741 (MH^+, $C_{16}H_{19}BrN_3O^+$; calc. 348.0711).

Data of **50c**: Brown solid. M.p. 156–158° ([49]: 156–157°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.20 (*t*, *J* = 7.2, 12 H); 3.41 (*q*, *J* = 7.2, 8 H); 6.64 (*d*, *J* = 9.6, 2 H); 6.68 (*d*, *J* = 9.3, 2 H); 8.12 (*d*, *J* = 9.3, 2 H); 8.27 (*d*, *J* = 9.6, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 12.6; 12.7; 44.5; 44.7; 109.9; 110.1; 110.5; 123.3; 128.1; 134.1; 149.1; 150.1.

Reaction between **48b** *and* **49a**. According to *Procedure A*, **48b** (508 mg, 1.87 mmol), **49a** (200 mg, 1.87 mmol), and Bu_4NF on SiO_2 (85 mg, 93 µmol) in THF (10 ml) gave *1-(3-chlorophenyl)-2-phenyldiazene* (**51d**; 50 mg, 12%), *1-(3-chlorophenyl)-2-phenyldiazene 2-oxide* (**52d**; 70 mg, 16%), **50a** (30 mg, 16%), and 3-chloroaniline (30 mg, 25%).

Data of **51d**: Bright orange solid. M.p. 68–70° ([50]: 68–69°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.47 (*m*, 2 H); 7.52 (*m*, 3 H); 7.83 (*m*, 1 H); 7.92 (*m*, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz): 121.6; 122.2; 122.9; 129.0; 130.1; 130.5; 131.3; 135.0; 152.1; 153.2.

Data of **52d**: Orange solid. M.p. 53–55° ([47]: 53–54°). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.42 (*m*, 2 H); 7.56 (*m*, 3 H); 7.98 (*ddd*, *J* = 7.5, 1.5, 1.2, 1 H); 8.25 (*dd*, *J* = 1.5, 1.2, 1 H); 8.29 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 122.2; 123.7; 125.1; 128.7; 129.3; 129.5; 131.8; 134.1; 144.7; 147.9.

Reaction between **48c** *and* **49a**. According to *Procedure B*, **49a** (123 mg, 1.15 mmol), **48c** (280 mg, 1.15 mmol), and MeOK (81 mg, 1.15 mmol) in THF (6 ml) gave **50a** (80 mg, 70%).

Reaction between **48c** *and* **49c**. According to *Procedure B*, **49c** (205 mg, 1.15 mmol), **48c** (280 mg, 1.15 mmol), and MeOK (81 mg, 1.15 mmol) in THF (6 ml) gave **50c** (120 mg, 61%).

Hexacarbonyl{μ²-[(1,2-η:1,2-η)-1-(tert*-butyl)-2-nitrosoacetylene]}dicobalt* (**58**). Isoamyl nitrite (740 μl, 645 mg, 5.51 mmol) and Me_3SiCl (700 μl, 599 mg, 5.51 mmol) were heated for 30 min at 40° under a gentle stream of Ar, and the brown NOCl gas that evolved was collected in a flask cooled to −78°. A soln. of **54** [51] (500 mg, 1.38 mmol) in CH_2Cl_2 (20 ml) at −70° was then transferred into the cold NOCl, and a green color appeared immediately. After stirring for 15 min at this temp., a soln. of $[Co_2(CO)_8]$ (521 μl, 942 mg, 2.76 mmol) in CH_2Cl_2 (10 ml) was added slowly, leading to immediate gas evolution. The mixture was stirred for 2 h while warming from −70° to 20°, and was then filtered over *Celite* and concentrated *in vacuo* to yield 400 mg of a dark brown solid. Purification (CC; hexane) afforded **58** (270 mg, 49%). Brown solid that slowly decomposes in soln. M.p. 80–83°(dec.). IR (CCl_4): 1456*w*, 2020*s*, 2950*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.3 (br. *s*, 9 H). Due to the instability of the soln., an acceptable ^{13}C-NMR spectrum could not be recorded.

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REFERENCES

[1] M. Irie, *Chem. Rev.* **2000**, *100*, 1685; 'Molecular Switches', Ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001.

[2] M. Fukushima, T. Osa, A. Ueno, *Chem. Lett.* **1991**, 709; K. R. A. S. Sandanayake, S. Shinkai, *J. Chem. Soc., Chem. Commun.* **1994**, 1083; S. Shinkai, in 'Comprehensive Supramolecular Chemistry', Vol. 1, Ed. G. W. Gokel, Pergamon-Elsevier, Oxford, 1996, p. 671–700; C. J. Ward, P. Patel, P. R. Ashton, T. D. James, *Chem. Commun.* **2000**, 229.

[3] G. S. Kumar, D. C. Neckers, *Chem. Rev.* **1989**, *89*, 1915; A. Izumi, R. Nomura, T. Masuda, *Macromolecules* **2001**, *34*, 4342.

[4] D.-L. Jiang, T. Aida, *Nature* **1997**, *388*, 454; A. Archut, G. C. Azzellini, V. Balzani, L. De Cola, F. Vögtle, *J. Am. Chem. Soc.* **1998**, *120*, 12187; D. M. Junge, D. V. McGrath, *J. Am. Chem. Soc.* **1999**, *121*, 4912; D. Patton, M.-K. Park, S. Wang, R. C. Advincula, *Langmuir* **2002**, *18*, 1688.

[5] H. Zollinger, 'Azo and Diazo Chemistry', Interscience, New York, 1961; S. Malkin, E. Fischer, *J. Phys. Chem.* **1962**, *66*, 2482.

[6] J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, O. C. Zafiriou, in 'Organic Photochemistry', Vol. 3, Ed. O. L. Chapman, Marcel Dekker, New York, 1973, p. 1–113; D. H. Waldeck, *Chem. Rev.* **1991**, *91*, 415; H. Meier, *Angew. Chem.* **1992**, *104*, 1425; *Angew. Chem., Int. Ed.* **1992**, *31*, 1399.

[7] R. E. Martin, J. Bartek, F. Diederich, R. R. Tykwinski, E. C. Meister, A. Hilger, H. P. Lüthi, *J. Chem. Soc., Perkin Trans. 2* **1998**, 233.

[8] F. Diederich, *Chem. Commun.* **2001**, 219; L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem.* **1999**, *111*, 737; *Angew. Chem., Int. Ed.* **1999**, *38*, 674; L. Gobbi, P. Seiler, F. Diederich, V. Gramlich, *Helv. Chim. Acta* **2000**, *83*, 1711; L. Gobbi, P. Seiler, F. Diederich, V. Gramlich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **2001**, *84*, 743.

[9] R. R. Tykwinski, M. Schreiber, R. P. Carlon, F. Diederich, V. Gramlich, *Helv. Chim. Acta* **1996**, *79*, 2249; R. R. Tykwinski, M. Schreiber, V. Gramlich, P. Seiler, F. Diederich, *Adv. Mater.* **1996**, *8*, 226.

[10] F. Diederich, Y. Rubin, C. B. Knobler, R. L. Whetten, K. E. Schriver, K. N. Houk, Y. Li, *Science* **1989**, *245*, 1088; F. Diederich, Y. Rubin, O. L. Chapman, N. S. Goroff, *Helv. Chim. Acta* **1994**, *77*, 1441.

[11] K. C. Nicolaou, W. M. Dai, *Angew. Chem.* **1991**, *103*, 1453; *Angew. Chem., Int. Ed.* **1991**, *30*, 1387; K. C. Nicolaou, A. L. Smith, in 'Modern Acetylene Chemistry' Eds. P. J. Stang, F. Diederich, VCH, Weinheim, 1995, p. 203–283; A. L. Smith, K. C. Nicolaou, *J. Med. Chem.* **1996**, *39*, 2103; E. Kraka, D. Cremer, *J. Am. Chem. Soc.* **2000**, *122*, 8245.

[12] R. R. Jones, R. G. Bergman, *J. Am. Chem. Soc.* **1972**, *94*, 660.
[13] J. Hoffner, M. J. Schottelius, D. Feichtinger, P. Chen, *J. Am. Chem. Soc.* **1998**, *120*, 376.
[14] a) W. M. David, S. M. Kerwin, *J. Am. Chem. Soc.* **1997**, *119*, 1464; b) C. J. Cramer, *J. Am. Chem. Soc.* **1998**, *120*, 6261; c) A. K. Nadipuram, W. M. David, D. Kumar, S. M. Kerwin, *Org. Lett.* **2002**, *4*, 4543; d) W. Tuntiwechapikul, W. M. David, D. Kumar, M. Salazar, S. M. Kerwin, *Biochemistry* **2002**, *41*, 5283; e) L. Feng, D. Kumar, S. M. Kerwin, *J. Org. Chem.* **2003**, *68*, 2234; f) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem.* **2003**, *115*, 518; *Angew. Chem., Int. Ed.* **2003**, *42*, 502.
[15] A. M. Sladkov, L. Y. Ukhin, G. N. Gorshkova, *Zh. Org. Khim.* **1966**, *2*, 1456; S. J. Huang, V. Paneccasio, F. DiBattista, D. Picker, G. Wilson, *J. Org. Chem.* **1975**, *40*, 124.
[16] R. Helwig, M. Hanack, *Chem. Ber.* **1985**, *118*, 1008.
[17] R. A. Yunes, A. J. Terenzani, L. do Amaral, *J. Am. Chem. Soc.* **1975**, *97*, 368.
[18] R. D. Little, G. L. Carroll, *J. Org. Chem.* **1979**, *44*, 4720.
[19] M. Squillacote, J. De Felippis, Y. L. Lai, *Tetrahedron Lett.* **1993**, *34*, 4137; M. Squillacote, J. De Felippis, *J. Org. Chem.* **1994**, *59*, 3564.
[20] a) K. Rüfenacht, *Helv. Chim. Acta* **1968**, *51*, 518; b) E. J. Corey, B. B. Snider, *J. Org. Chem.* **1973**, *38*, 3632; c) S. W. Mojé, P. Beak, *J. Org. Chem.* **1974**, *39*, 2951.
[21] P. J. Stang, B. W. Surber, Z.-C. Chen, K. A. Roberts, A. G. Anderson, *J. Am. Chem. Soc.* **1987**, *109*, 228; P. J. Stang in 'Modern Acetylene Chemistry', Eds. P. J. Stang, F. Diederich, VCH, Weinheim, 1995, p. 67–97.
[22] B. Witulski, T. Stengel, *Angew. Chem.* **1998**, *110*, 495; *Angew. Chem., Int. Ed*. **1998**, *37*, 489; B. Witulski, M. Gössmann, *Synlett* **2000**, 1793.
[23] a) E. J. Corey, W. L. Mock, *J. Am. Chem. Soc.* **1962**, *84*, 685; b) S. F. Nelsen, *J. Am. Chem. Soc.* **1974**, *96*, 5669; c) L. A. Carpino, R. E. Padyluka, D. E. Barr, F. H. Hall, J. G. Krause, R. F. Dufresne, C. J. Thoman, *J. Org. Chem.* **1988**, *53*, 2565.
[24] J. Balsells, J. Vazquez, A. Moyano, M. A. Pericas, A. Riera, *J. Org. Chem.* **2000**, *65*, 7291.
[25] S. Hayat, A. Rahman, M. I. Choudhary, K. M. Khan, W. Schumann, E. Bayer, *Tetrahedron* **2001**, *57*, 9951.
[26] D. S. Malament, N. Levi, *J. Org. Chem.* **1975**, *40*, 3285.
[27] R. Appel, B. Blaser, G. Siegemund, *Z. Anorg. Allg. Chem.* **1968**, *363*, 176; R. Appel, B. Blaser, R. Kleinstück, K.-D. Ziehn, *Chem. Ber.* **1971**, *104*, 1847.
[28] R. A. Ruden, *J. Org. Chem.* **1974**, *39*, 3607.
[29] a) M. A. Pericas, F. Serratosa, E. Valenti, *Tetrahedron* **1987**, *43*, 2311; b) E. Valenti, M. A. Pericas, F. Serratosa, *J. Org. Chem.* **1990**, *55*, 395.
[30] J. K. Crandall, L. C. Crawley, *J. Org. Chem.* **1974**, *39*, 489; T. Hirao, K. Hayashi, J. Motoyoshiya, Y. Ohshiro, T. Agawa, *Chem. Lett.* **1981**, 1197; M. S. Novikov, A. F. Khlebnikov, R. R. Kostikov, *Zh. Org. Khim.* **1991**, *27*, 1794.
[31] A. Z. Rubezhov, E. R. Milaeva, A. I. Prokof'ev, I. V. Karsanov, O. Y. Okhlobystin, *Izv. Akad. Nauk SSSR, Ser. Kh.* **1984**, 1143; J. D. Perez, D. A. Wunderlin, T. L. Lemke, K. N. Sawhney, *J. Heterocycl. Chem.* **1987**, *24*, 1073.
[32] J. Schweng, E. Zbiral, *Monatsh. Chem.* **1976**, *107*, 537.
[33] P. L. Coe, A. Sellars, J. C. Tatlow, *J. Chem. Soc., Perkin Trans. 1* **1985**, 2185.
[34] A. S. Yim, M. H. Akthar, A. M. Unrau, A. C. Oehlschlager, *Can. J. Chem.* **1978**, *56*, 289.
[35] a) H. Zimmer, G. Singh, *Angew. Chem.* **1963**, *75*, 574; *Angew. Chem., Int. Ed.* **1963**, *2*, 395; b) R. Weiss, K.-G. Wagner, M. Hertel, *Chem. Ber.* **1984**, *117*, 1965; c) R. M. Alvarez, M. Hanack, T. Schmid, L. R. Subramanian, *J. Phys. Org. Chem.* **1995**, *8*, 191.
[36] S. Sakaue, T. Tsubakino, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* **1993**, *58*, 3633; Y. Mugnier, J.-C. Gard, Y. Huang, Y. Couture, A. Lasia, J. Lessard, *J. Org. Chem.* **1993**, *58*, 5329; E. Steudel, J. Posdorfer, R. N. Schindler, *Electrochim. Acta* **1995**, *40*, 1587.
[37] D. A. Fletcher, B. G. Gowenlock, K. G. Orrell, *J. Chem. Soc., Perkin Trans 2* **1998**, 797.
[38] Y. Ogata, J. Mibae, *J. Org. Chem.* **1962**, *27*, 2048.
[39] a) R. H. Weigmann, E.-U. Würthwein, *Tetrahedron Lett.* **1989**, *30*, 6147; b) F. D. King, D. R. M. Walton, *Synthesis* **1975**, 788; c) E. Robson, J. M. Tedder, D. J. Woodcock, *J. Chem. Soc. C* **1968**, 1324.
[40] M. O. Frederick, J. A. Mulder, M. R. Tracey, R. P. Hsung, J.-J. Huang, K. C. M. Kurtz, L. Shen, C. J. Douglas, *J. Am. Chem. Soc.* **2003**, *125*, 2368.
[41] T. Koenig, W. R. Mabey, *J. Am. Chem. Soc.* **1970**, *92*, 3804; T. Koenig, M. Deinzer, J. A. Hoobler, *J. Am. Chem. Soc.* **1971**, *93*, 938; T. Koenig, J. A. Hoobler, W. R. Mabey, *J. Am. Chem. Soc.* **1972**, *94*, 2514.
[42] G. D. Mendenhall, *Tetrahedron Lett.* **1983**, *24*, 451; E. M. Y. Quinga, G. D. Mendenhall, *J. Org. Chem.* **1985**, *50*, 2836.

[43] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[44] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures. University of Göttingen, Germany, 1997.
[45] S. V. Ponomarev, A. S. Zolotareva, R. N. Ezhov, Y. V. Kuznetsov, V. S. Petrosyan, *Russ. Chem. Bull.* **2001**, *50*, 1093.
[46] H.-J. Cristau, E. Manginot, E. Torreilles, *Synthesis* **1991**, 382.
[47] M. Okubo, K. Koga, *Bull. Chem. Soc. Jpn*. **1983**, *56*, 203.
[48] L. C. Behr, *J. Am. Chem. Soc*. **1954**, *76*, 3672.
[49] K. Zieloff, H. Paul, G. Hilgetag, *J. Prakt. Chem.* **1966**, *31*, 200.
[50] W. F. Little, A. K. Clarke, *J. Org. Chem.* **1960**, *25*, 1979.
[51] J. R. Johnson, W. L. McEwen, *J. Am. Chem. Soc.* **1926**, *48*, 469.

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