

The Behaviors of Metal Acetylides with Dinitrogen Tetroxide

by Christopher J. Woltermann and Harold Shechter*

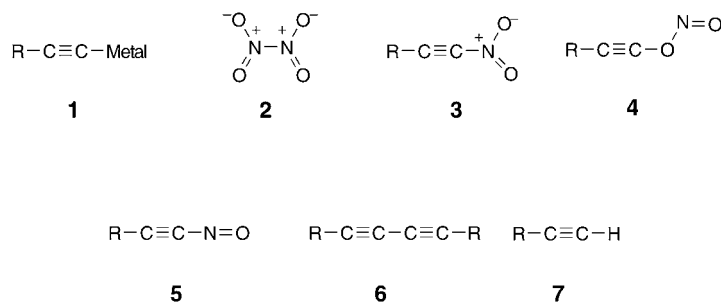
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Lithium phenylacetylide (**1a**) and N_2O_4 (**2**) at -78° yield diphenylbutadiyne (**6a**) by oxidative coupling, phenylacetylene (**7a**) by oxidation and then solvent H-abstraction, and benzoyl cyanide (**8**) by dimerizative-rearrangement of nitroso(phenyl)acetylene (**23**). Nitro(phenyl)acetylene (**3**, R = Ph) is not obtained. Benzonitrile (**9**), a further product, possibly results from hydrolytic decomposition of nitroso(phenyl)ketene (**27**) generated from phenylacetylenyl nitrite (**26**). Phenylacetylene (**7a**) and **2** give, along with (*E*)- and (*Z*)-1,2-dinitrostyrenes (**34** and **35**, resp.), 3-benzoyl-5-phenylisoxazole (**10**), presumably as formed by cycloaddition of benzoyl nitrile oxide (**40**) to **7a**. Further, **2** reacts with other lithium acetylides (**1b–1e**), and with sodium, magnesium, zinc, copper, and copper lithium phenylacetylides, **1f–1i**, to yield diacetylenes **6a–6c** and monoacetylenes **7a–7c**. Conversions of metallo acetylide aggregates to diacetylenes are proposed to involve generation and addition reactions of metallo acetylide radical cationic intermediates in cage, further oxidation, and total loss of metal ion. Loss of metal ions from metallo acetylide radical cations and H-abstraction by non-caged acetylenyl radicals will give terminal acetylenes. The principal reactions (75–100%) of heavy metal acetylides phenyl(trimethylstannyl)acetylene (**44**) and bis(phenylacetylenyl)mercury (**47**) with **2** are directed nitrosative additions (NO^+) and loss of metal ions to give nitroso(phenyl)ketene (**27**), which converts to benzoyl cyanide (**8**).

Introduction. – The present study primarily involves the behaviors of metal acetylides (**1**) with dinitrogen tetroxide (N_2O_4 ; **2**). Of interest is determination if **1** reacts with **2** to give 1) 1-nitroacetylenes (**3**) [1][2], 1-acetylenyl nitrites (**4**), and/or 1-nitrosoacetylenes (**5**) [3], 2) conjugated diacetylenes **6** by oxidative coupling¹⁾ [4], and/or 3) monoacetylenes **7** by oxidation of **1** and then abstraction of hydrogen. Literature methods for syntheses of nitro- and nitrosoacetylenes **3** [1][2] and **5** [3]²⁾, respectively, are unsatisfactory; acetylenyl nitrites **4** are unknown. Investigation has also been made of 1) other products formed from **1** and **2**, and 2) the reactions of **2** with phenylacetylene (**7**, R = Ph):

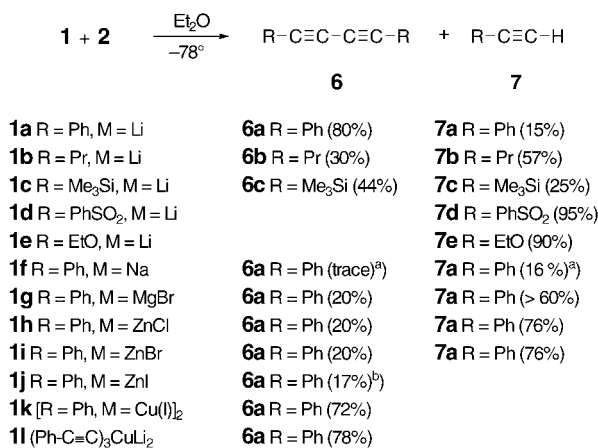
Results and Discussions. – Addition of N_2O_4 (**2**; 1 equiv.) in Et_2O to lithium phenylacetylide (**1a**) in Et_2O at -78° (*Scheme 1*) and direct analysis of the reaction products by GC/MS/IR reveal that diphenylbutadiyne (**6a**; 80%) and phenylacetylene (**7a**; 15%) are obtained. In experiments conducted as above at -78° in which the solvent is hexane, **1a** and **2** yield phenylacetylene **7a** (95%), and diacetylene **6a** is not found. Reactions of **2** with **1a** at -78° in *Fluorinert*, a perfluoroalkane solvent, give

- ¹⁾ For recent review and references concerning oxidative coupling of metal acetylides (**1**) to diacetylenes (**6**), see [4].
- ²⁾ Reference [2] reports that ‘addition of nitronium salts to a lithio acetylide does not give a nitroacetylene’. The products of these reactions were not given.



diacetylene **6a** (75%) and polar products, but no phenylacetylene (**7a**), nitro(phenyl)acetylene (**3**, R = Ph) [**1a**], or nitroso(phenyl)acetylene (**5**, R = Ph) [3]. In further efforts to determine if **3** (R = Ph) is obtained from **1a** and **2** in Et₂O at -78°, Et₂NH was added to the cold reaction mixtures within 10 min after introduction of **2** had been completed. *Michael* adducts (*E*)- and (*Z*)-(Et₂)N-C(Ph)=CH-NO₂ and derivatives thereof containing NO₂ groups are not found³).

Scheme 1



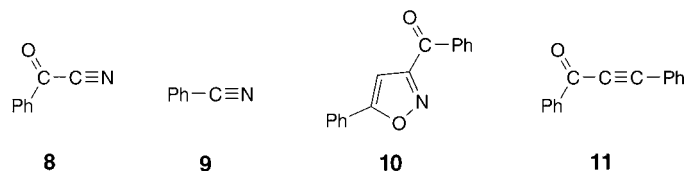
^{a)} Isoxazole **10** and (*E*)- and (*Z*)-1,2-dinitrostyrenes (**34** and **35**) are major products.

^{b)} Iodo(phenyl)acetylene is obtained in 74% yield.

The products and yields obtained from **1a** and **2** in a specific solvent depend on the order and the rates of addition and mixing of the reactants, temperature, and reaction time. Rapid addition of **1a** in Et₂O to **2** in Et₂O at -78° and direct GC/MS/IR analysis of the cold reaction mixture reveal monoacetylene **7a** (60%) and diacetylene **6a** (13%) to be the volatile products. Slow addition of **1a** in Et₂O to excess **2** in Et₂O at 0°, rapid aqueous washing of the cold reaction mixture, and product isolation by rapid column chromatography yield diacetylene **6a** (>25%), benzoyl cyanide (**8**; >5%), benzonitro-

³⁾ Et₂NH adds to 3,3-dimethyl-1-nitrobut-1-yne at 0° to give 2-(diethylamino)-3,3-dimethyl-1-nitrobut-1-enes (94%) [5].

trile (**9**; > 3%, [6b]), 3-benzoyl-5-phenylisoxazole (**10**; > 15%, [6c]), and non-volatile polar materials. Products **8**–**10** are always found in reactions in which **1a** is added to **2** in Et₂O. Use of interface reaction techniques [7] in which **2** in THF is solidified on top of a **1a**/THF glass at –196°, and the solid mixture is melted slowly yield **7a** and **8** as major products along with benzoyl(phenyl)acetylene (**11**) and high-molecular weight materials. Acetylene **11**, identified by comparison with an authentic sample, is presumably formed by displacement of cyanide ion in reaction of **8** with **1a**. Condensation of **2** on solid **1a** [7] at –196° results in violent reactions.

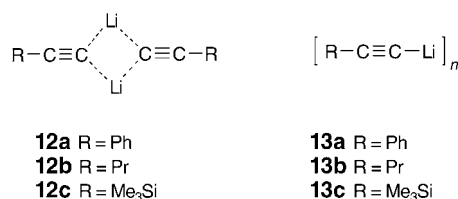


The behaviors of other lithium acetylides **1b**–**1e** (Scheme 1) with N₂O₄ (**2**) have also been investigated. Addition of **2** (1 equiv.) in Et₂O to lithium pent-1-yne (**1b**) in Et₂O at –78° and rapid direct GC/MS/IR analysis of the reaction mixture reveal that deca-4,6-diyne (**6b**; 30%) and pent-1-yne (**7b**; 57%) are produced. Similarly, lithium trimethylsilylacetylide (**1c**) and **2** yield 1,4-bis(trimethylsilyl)buta-1,3-diyne (**6c**; 44%) and (trimethylsilyl)acetylene (**7c**; 25%); 1-nitro-2-(trimethylsilyl)acetylene (**3**; R = Me₃Si) [2] is not found. Since 1-nitro-2-(triisopropylsilyl)acetylene [2] decomposes violently in air at ca. 200° to give 1,4-bis(triisopropylsilyl)buta-1,3-diyne (50%) and ·NO₂, the possibility that **3** (R = Me₃Si) is formed in reactions of **1c** and **2** in Et₂O at –78° and is then converted to **6c** was of concern. The behavior of **3** (R = Me₃Si) prepared independently [2] has, thus, been investigated in detail. The nitro(silyl)acetylene can be chromatographed satisfactorily (TLC and GC) and does not yield **6c** under the varied conditions of the present experiments. Further, lithium (phenylsulfonyl)acetylide (**1d**) and lithium ethoxyacetylide (**1e**) react selectively with **2** at –78° in Et₂O to give (phenylsulfonyl)acetylene (**7d**; 95%) and ethoxyacetylene (**7e**; 90%), respectively; diacetylenes are not obtained. In none of the above experiments is a nitroacetylene (**3**), nitrosoacetylene (**5**), acetylenyl nitrite (**4**), or an acetylenyl nitrate (R–C≡C–ONO₂) detected.

The mechanisms of the reactions of **2** with lithium acetylides (**1**; Metal = Li) in various solvents are of interest. Solid **2** is planar and of structure indicated [8a]. Unhindered ethers form adducts with **2** [8b]. Et₂O and **2** yield N₂O₄·2 Et₂O (m.p. –74.8°), THF and **2** give 2 adducts: N₂O₄·C₄H₈O (m.p. –20.5°) and N₂O₄·2 C₄H₈O (incongruent m.p.), and dioxane and **2** form N₂O₄·O(CH₂CH₂)₂O (m.p. 45.2°) [8b]. The magnetic moments and the Raman, VIS, and IR spectra of solutions of **2** in ethers at –72° to –55° reveal that the N₂O₄ (**2**) is only slightly dissociated into ·NO₂, NO⁺, and NO₃[–], or NO₂[·] and NO₂[–] [8c–j]. At its boiling point (21.5°) at atmospheric pressure, **2** is 0.12% dissociated into ·NO₂ [8h]. The equilibrium constants for decomposition of **2** into ·NO₂ in C₆H₁₂, CCl₄, and MeCN at 25° are 1.77 × 10^{–4}, 1.78 × 10^{–4}, and 3 × 10^{–5} mol l^{–1}, respectively [8i]. There is much less dissociation of **2** into NO₂[·] and NO₂[–] than into NO⁺ and NO₃[–] in the above solvents [8j]. There is much chemistry, however, in which **2** in ethers and in various non-polar solvents at higher temperatures, possibly

via ONONO_2 (*syn* and *anti*) [9a], is a source of 1) the nitrosonium ion (NO^+) which functions as an electron transfer [9b] or/and a nitrosating agent [9b] and 2) $\cdot\text{NO}_2$ for varied homolytic reactions.

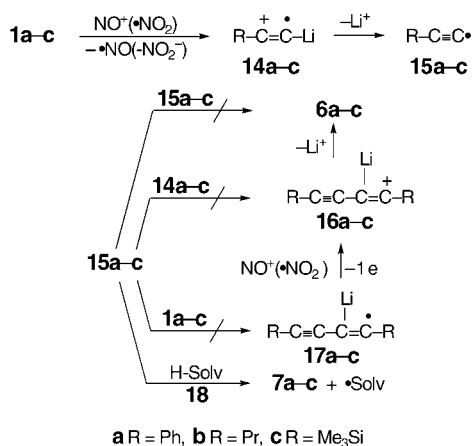
As is known for many alkyl, alkenyl, and aryllithium reagents, lithium acetylides are aggregates [10][11]. Lithium phenylacetylide (**1a**) is a four-membered ring dimer, **12a**, in THF at -78° and oligomeric, **13a**, as a solid [11a–c]. Lithium *tert*-butylacetylide is a cyclic dimer, **12** ($\text{R} = t\text{-Bu}$), in hexane, forms the tetramer $[\text{t-Bu-C}\equiv\text{C-Li}]_4(\text{THF})_4$ [11d,e] and the dodecamer $[\text{t-Bu-C}\equiv\text{C-Li}]_{12}(\text{THF})_4$ [11d] with THF, and is oligomeric, **13** ($\text{R} = t\text{-Bu}$), when dry [11d]. Presumably lithium acetylides **1b** and **1c** are self-associated in Et_2O , hydrocarbons, and perfluorinated solvents before initiation of their reactions with **2** at low temperatures. The lithium [10][11] in aggregates **12** and **13** is also coordinated with Et_2O and other donor solvents, but such interactions are not included in representations such as **12** and **13**, or in the simplified mechanistic schemes and equations in this summary.



Production of diacetylenes **6a–6c** and monoacetylenes **7a–7c** from **1a–1c** and **2** at -78° in various solvents raises significant mechanistic questions. Oxidations of solvated aggregates of **1a–1c** (*Scheme 2*) are envisaged to involve additions of NO^+ or $\cdot\text{NO}_2$ to the $\text{C}\equiv\text{C}$ bonds of the lithium acetylides and loss of $\cdot\text{NO}$ or NO_2^- and/or direct electron transfers to NO^+ and/or $\cdot\text{NO}_2$ from the acetylene π electron systems, C-Li bonds or bonded Li-atoms in **1a–1c** in cage to give solvated-caged and then (or) non-caged lithium acetylide radical cations **14a–14c**, respectively. Hybrid representations of non-caged monomeric **14a–14c** are $\text{R}-\overset{\cdot}{\text{C}}=\overset{\oplus}{\text{C}}-\text{Li}$ and $[\text{R}-\text{C}\equiv\text{C}\cdot\text{Li}]^+$. Loss of Li^+ from non-caged **14a–14c** will yield discrete 1-acetylenyl radicals **15a–15c**. Formation of diacetylenes **6a–6c** (*Scheme 2*) as major products, however, by 1) direct couplings of discrete acetylenyl radicals **15a–15c**, respectively, 2) additions of **15a–15c** to radical cations **14a–14c** to give 2-lithiobut-1-en-3-ynyl cations **16a–16c**, respectively, and then loss of Li^+ , and/or 3) reactions of discrete radicals **15a–15c** with **1a–1c** to yield 2-lithiobut-1-en-3-ynyl radicals **17a–17c**, respectively, followed by oxidation (single-electron transfer), and Li^+ loss is highly unlikely because of the low concentrations and the great solvent H-abstraction reactivities predicted for discrete acetylenyl radicals **15a–15c** [12]⁴). Reactions of radicals **15a–15c** to produce or leading to diacetylenes **6a–6c** (*Scheme 2*) in high yields would have to take place rapidly in tight cages and not involve **2** or the solvents. Production of monoacetylenes **7a–7c** in the above experiments presumably results (*Scheme 2*) by H-abstraction from H-containing

⁴) Because of the great strengths of acetylenic C–H bonds (*ca.* 125 kcal/mol), uncomplexed acetylenyl free radicals such as **15a–15c** are expected to react rapidly with ethers and with hydrocarbon solvents at -78° with H-abstraction at rates of near-diffusional control [12].

Scheme 2

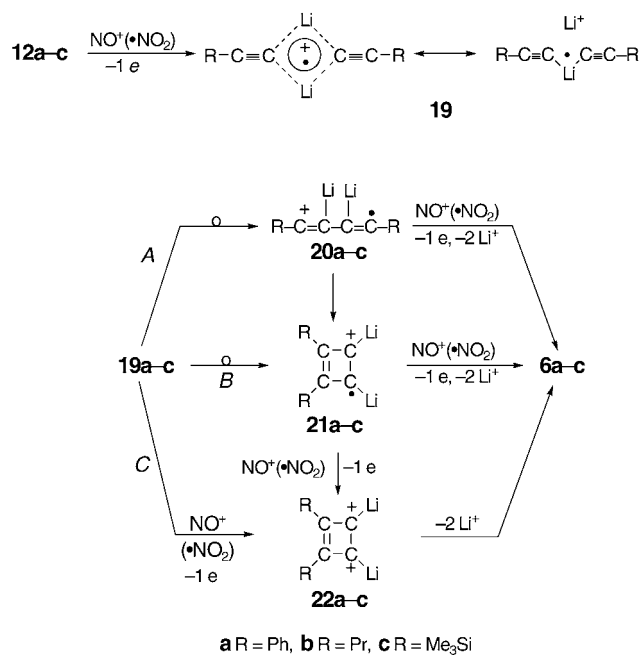


solvents, **18**, by the non-caged, highly reactive acetylenyl radicals **15a–15c** eventually generated⁴).

Production of diacetylenes **6a–6c** in reactions of **1a–1c** with **2** is explained by oxidation (overall one electron transfer to ^+NO and/or $\cdot\text{NO}_2$) of a lithium acetylide unit in each of the cyclic dimers **12a–12c** (Scheme 3) to give caged, highly delocalized, radical-cationic reaction intermediates **19a–19c**. Reorganizations of **19a–19c** may then occur (Scheme 3) to yield 2,3-dilithiobuta-1,3-diene (Sequence A) or/and 1,2-dilithiocyclobutadiene radical cation intermediates [13] (Sequence B), **20a–20c** and **21a–21c**, respectively, which undergo oxidation (overall one-electron transfer to ^+NO and/or $\cdot\text{NO}_2$) and loss of 2Li^+ . Dilithiocyclobutadiene radical cations **21a–21c** in cage are expected to be highly delocalized and may be of lower energies than their isomeric dilithiobuta-1,3-diene radical cations **20a–20c**. Support for Sequence B of Scheme 3 is that acetylene radical cations ($\text{R}-\overset{\cdot}{\text{C}}=\overset{+}{\text{C}}-\text{R}$) add to acetylenes ($\text{R}-\text{C}\equiv\text{C}-\text{R}$) at low temperatures to give long-lived cyclobuta-1,3-diene radical cation analogs of **21a–21c** efficiently [13a][13b], and that such cyclobutadiene radical cations, **21a–21c** (H instead of Li), in gaseous and condensed phases are theorized to be more stable than their buta-1,3-diene radical cation isomers **20a–20c** (H instead of Li) [13c]. Oxidations (one-electron transfer) of lithio radical cations **14a–14c** in cage resulting in cyclo-dimerizations (Scheme 3, Sequence C) and/or oxidations (one-electron transfer) of **21a–21c** may yield stabilized 1,2-dilithiocyclobutadiene dication intermediates **22a–22c**⁵) [14], which upon loss of 2Li^+ give **6a–6c**. Mechanisms similar to those in Scheme 3 also explain oxidative transformations of higher aggregates of **1a–1c** by **2** to diacetylenes **6a–6c**. Conversions of lithium acetylides **1d** and **1e** in Et_2O at -78° (Scheme 1) by **2** almost totally to monoacetylenes **7d** (95%) and **7e** (90%), respectively, imply that lithium acetylide radical cation intermediates **14** ($\text{R} = \text{EtO}$ and PhSO_2) as generated by

⁵) For discussions of the structures, stabilities, and theory of cyclobutadiene dication intermediates, see [14] and refs. cit. therein.

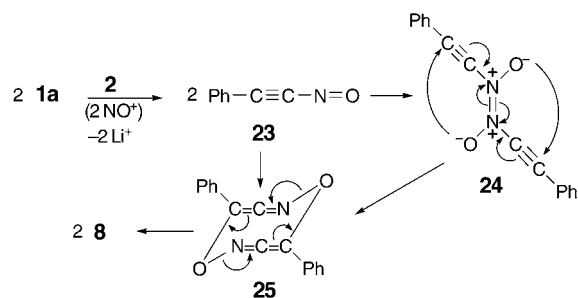
Scheme 3



oxidation are not held tightly in aggregates, or/and the subsequent acetylenyl radicals **15** (R = EtO and PhSO₂) are not as complexed by Li⁺ as those from **1a–1c** and thus **1d** and **1e** are proposed to react with **2** as in *Scheme 2*.

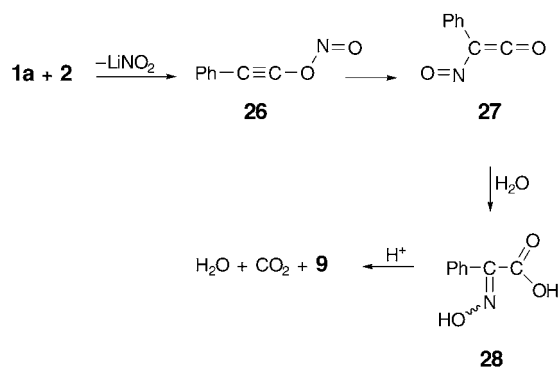
Reaction of **1a** and **2** to give benzoyl cyanide (**8**) is understandable (*Scheme 4*). Metal alkylmonoacetylides (R–C≡C–M; R = *t*-Bu and Bu and M = Hg and Li) are known to react with nitrosyl chloride (NOCl) at –78° in CH₂Cl₂ to give nitrosoacetylides **5** as unstable products (which have been detected spectroscopically) that convert to acyl cyanides (R–CO–CN) on warming [3]. Many nitroso compounds (R–N=O) dimerize rapidly to (*E*)- and (*Z*)-azo-*N,N'*-dioxides R–NO=NO–R [15].

Scheme 4

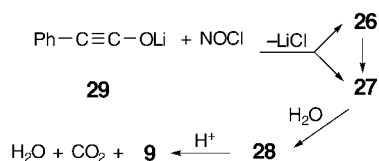


Formation of **8** from **1a** and **2** is rationalized (*Scheme 4*) by nitrosation of **1a** by NO^+ (by directed addition–elimination and/or displacement) to give nitroso(phenyl)acetylene (**23**), which dimerizes to (*E*)-**24** that then converts to **25**. Dimerization of **23** (*Scheme 4*) might also give **25** directly. Collapse of cyclodimer **25** as illustrated in *Scheme 4* will then yield acyl cyanide **8**. Unimolecular rearrangement of **23** to **8** is presumed to be a less-likely process.

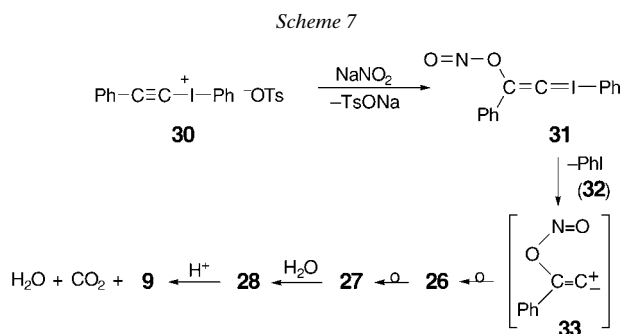
That benzonitrile (**9**) is obtained from lithium phenylacetylide (**1a**) (and many other metal phenylacetylides) and **2** under varied conditions led to speculation and study. Of interest is whether **1a** and **2** (*Scheme 5*) react to give phenylacetylenyl nitrite (**26**) that isomerizes to nitroso(phenyl)ketene (**27**) which, upon reaction with H_2O and then decomposition of the (*E*)- and (*Z*)-phenylglyoxylic acid oximes (**28**) generated, yields **9**. Nitrosoketene ($\text{O}=\text{N}-\text{CH}=\text{C}=\text{O}$) has been prepared [16]. As noted previously, acetylen-1-yl nitrites (**4**) have not been reported. In present experiments, all attempts (*Scheme 5*) to prepare or detect acetylenyl nitrite **26** or nitrosoketene **27** by varied preparative-separation methods and/or rapid direct gas-chromatographic analyses of the products from **1a** and **2** at -78° were unsuccessful. Phenylglyoxylic acid oximes **28** (*Scheme 5*), however, do convert rapidly in acidic environments to **9**, CO_2 , and H_2O [17].

Scheme 5

In efforts to prepare and determine the behavior of phenylacetylenyl nitrite (**26**) as in *Scheme 6*, lithium phenylethynolate (**29**) [18] and NOCl at -78° in Et_2O and rapid aqueous washing of the cold mixture are found to give PhCN (**9**) and CO_2 as major products. Acetylenyl nitrite **26** was not detected. Whether **29** reacts with NOCl to give nitrosoketene **27** directly or/and acetylenyl nitrite **26**, which rearranges to ketene **27** as in *Scheme 6*, cannot yet be concluded.

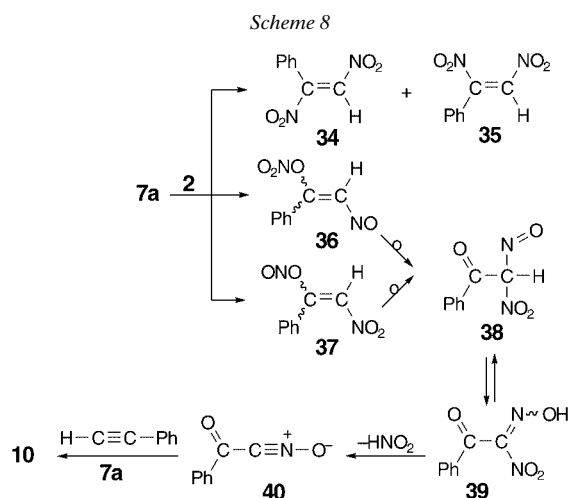
Scheme 6

In a further study of possible generation and the chemistry of phenylacetylenyl nitrite (**26**; *Scheme 7*), NaNO_2 is found to react with phenyl(phenylacetylenyl)iodonium toluene-4-sulfonate (**30**) [19a] upon phase transfer in $\text{H}_2\text{O}/\text{CHCl}_3$ with loss of TsONa , H_2O , and CO_2 to yield benzonitrile (**9**; > 45%) and iodobenzene (**32**; 81%). Addition–displacement of **30** (*Scheme 7*) by NO_2^- to form iodonium ylide **31**, which, upon loss of **32**, followed by rearrangement of carbene **33** to give acetylenyl nitrite **26**, is a sequence similar to that for **30** with other nucleophiles [19b]. Conversion of phenylacetylenyl nitrite (**26**) to nitrile **9** as in *Scheme 7* is identical to that presumed for **26** as generated from **1a** (*Scheme 5*) and from lithium phenylethyolate (**29**; *Scheme 6*).



Since phenylacetylene (**7a**) is a major product from **1a** and **2** (1 equiv.) in Et_2O and hydrocarbon solvents, and, as to be discussed, is expected to be involved in formation of isoxazole **10**, the behavior of **7a** with **2** has been investigated. Reactions of **7a** and **2** in Et_2O /gasoline at 0° are reported to yield (*E*)- and (*Z*)-1,2-dinitrostyrenes (**34** and **35**; *Scheme 8*); other products were not identified [20a]. Similarly, hex-3-yne and **2** in Et_2O at $0-10^\circ$ give (*Z*)- and (*E*)-3,4-dinitrohex-3-enes (4.5 and 35%, resp.) along with 4,4-dinitrohexan-3-one (8%), hexane-3,4-dione (8%), and propanoic acid (6%) [20b]. Pent-1-yne and **2** in Et_2O at $0-10^\circ$ yield unidentified products [20b]. In present experiments, phenylacetylene (**7a**) and **2** in Et_2O /ligroin at -78° yield 1,2-dinitrostyrenes **34** and **35** (42%; *Scheme 8*), isoxazole **10** (25%; *Scheme 8*), and other polar materials are, however, also obtained. Isoxazole **10** is possibly formed by [3 + 2] dipolar cycloaddition of phenylacetylene (**7a**) to benzoyl nitrile oxide (**40**) as generated from **7a** and **2** via adducts **36** or/and **37** [21], and then **38** and benzoyl methanenitric acid (**39**) as in *Scheme 8*. Nitrolic acids ($\text{R}-\text{C}(=\text{NOH})-\text{NO}_2$) undergo elimination of HNO_2 readily to form nitrile oxides ($\text{R}-\text{C}\equiv\text{N}^+-\text{O}^-$) [21]. Cycloadditions of nitrile oxides to acetylenes to give isoxazoles are well-established [21].

Investigation was then made of the behaviors of other metal phenylacetylides, **1f-1i**, with **2**. Sodium phenylacetylide (**1f**) is reported to undergo oxidative coupling to diacetylene **6a** (67%) by reaction with KMnO_4 in liquid NH_3 at -35° [22]. Rapid addition of **2** in Et_2O to **1f** suspended in Et_2O at -78° is now found to yield phenylacetylene (**7a**; 16%), (*E*)- and (*Z*)-1,2-dinitrostyrenes (**34** and **35**, resp. are major products), and isoxazole **10** (23%) along with diacetylene **6a** (low yield) and

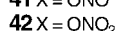
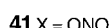
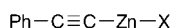


chromatographically unseparable materials. That there is much less conversion of **1f** than of **1a** by **2** in Et₂O at -78° to diacetylene **6a** is of interest.

Sodium acetylides Na-C≡C-H [23a] and Na-C≡C-CH₃ [23b] are tetrameric, layered aggregates with limited solubilities in Et₂O, hydrocarbon, and other non-polar solvents. Because of the greater electropositivity and size of Na⁺ as compared to Li⁺, sodium acetylides (**1**, M=Na) are expected to be more reactive than Li analogs. Sodium phenylacetylide aggregates **1f** are, thus, predicted to be oxidized more readily by NO⁺, ·NO₂, and/or **2**, and less subject to cage maintenance effects than is **1a**. Further, sodium phenylacetylenyl radical cations (Ph-C≡C^{•+}-Na) are expected to be less tightly metal-bonded and to decompose to discrete phenylacetylenyl radicals (**15a**) more readily than do lithio radical cation analogs **14a**. Reactions of **1f** with **2** to give more monoacetylene **7a** and much less diacetylene **6a** than do **1a** and **2** under comparable conditions are, thus, rationalized.

The behaviors of **2** with more covalent metal phenylacetylides (**1**) were then studied. Solid magnesium phenylacetylide/THF ((Ph-C≡C)₂Mg(THF)₄) [24], zinc phenylacetylide ((Ph-C≡C)₂Zn) [25a,b], and other zinc acetylide derivatives ((R-C≡C)₂Zn) [25c-f] are highly-bridged metal-acetylene aggregates. Alkynyl *Grignard* reagents are oxidatively homocoupled to diacetylenes by iodine [26a-c], Cu^{II} and Co^{II} salts [26c-f], nitrobenzene [26g], and oxovanadium(V) compounds (VO(OR)Cl₂) [26h], respectively. Phenylacetylenylmagnesium bromide (**1g**) [27] and **2** in Et₂O at -78° are now found to yield diacetylene **6a** (20%) and phenylacetylene (**7a**; >60%) along with cyanide **8**, nitrile **9**, and isoxazole **10**. Phenylacetylenylzinc chloride (**1h**) and phenylacetylenylzinc bromide (**1i**) in THF at -78° each also react with **2** on warming slowly (and rapid direct GC/MS/IR analyses of the mixtures) to give diacetylene **6a** (20%) and monoacetylene **7a** (76%). The principal reactions of **1g-1i**, respectively, with **2** in Et₂O apparently involve one-electron transfer from metallo-acetylene units in the organometallics, cage collapse to give discrete phenylacetylenyl radicals **15** (R=Ph), and H-abstraction similar to that in

*Scheme 2*⁶). In reactions with **2**, magnesium acetylide **1g**, and zinc acetylides **1h** and **1i** yield more coupling product diacetylene **6a** than does sodium acetylide **1f** but much less **6a** than does lithium acetylide **1a**. The divalent metal ions Mg⁺⁺ and Zn⁺⁺ presumably do not hold acetylide oxidation intermediates as tightly in cage as does Li⁺ in reactions of phenylacetylides **1g** and **1h** with **2** to give coupling product diacetylene **6a**. Phenylacetylenylzinc iodide (**1j**) is converted, however, by **2** in THF (–78°) to iodo(phenyl)acetylene (Ph–C≡C–I; 74%) along with diacetylene **6a** (17%). The iodide ion in the reaction mixture from **1j** and **2** is rapidly oxidized to iodine, which then reacts with **1j** or/and acetylenylzinc nitrite **41** and/or nitrate **42** to form iodo(phenyl)acetylene. Diacetylene **6a** is also produced from **1j** and **2** in significant yield presumably by oxidation–reduction (electron transfer) and subsequent reactions at –78° similar to that proposed for **1a** and **2** (*Scheme 3*). In none of the above experiments with **2** and **1g–1j**, respectively, was nitro(phenyl)acetylene (**3**, R = Ph) detected.



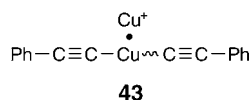
Copper(I) phenylacetylide (**1k**) [28] behaves differently from **1h** and **1i** with **2** in THF at –78° in that diacetylene **6a** (> 72%) is the major product. Phenylacetylene (**7a**), the H-abstraction product, is not found. Similarly, dilithium tris(phenylacetylenyl) cuprate (**1l**) reacts rapidly with **2** in Et₂O at –78° to give diacetylene **6a** (> 71%) and no **7a**. The behaviors of **1k** and **1l** with **2** are, thus, similar to conversions of varied copper acetylides (**1**, M = Cu) to diacetylenes **6** [4] in ammoniacal solution by oxygen [29a–c] and by Cu^{II} reagents [29d–h] in pyridine or amine bases, peroxides [29i–j], and potassium ferricyanide [29k,l]. Although oxidative couplings of copper acetylides are widely used for synthesis of conjugated diacetylenes, and the behaviors of such acetylides with oxygen and with cupric salts have been investigated kinetically and otherwise⁷), the detailed mechanisms of these reactions have not been established [4]. The present results with **2** and **1k** (and other metal acetylides) allow discussion [4] with respect to the mechanisms of the oxidative couplings.

Copper(I) phenylacetylide (**1k**) is a tight, high-molecular-weight oligomer of known structure [30]. The overall conversion of **1k** by **2** (and possibly O₂) to **6a** is presently explainable⁷) [4] by oxidation (one-electron transfer, 1 equiv.) of a dimer unit in the aggregate [30] to give the resulting delocalized cuprous bis(phenylacetylenyl) radical cation (**43**) in cage. Much as in the conversions of **12a–12c** to **6a–6c** in *Scheme 3*, intramolecular rearrangement of **43**, oxidation (one-electron transfer), and total loss of Cu⁺ and/or oxidation of **43**, cyclodimerization, and total loss of Cu⁺ will yield diacetylene **6a**. Mechanisms similar to the above may operate in oxidation of lithio cuprate **1l** by **2** to diacetylene **6a**. In the reactions of **1k** and of **1l** with **2** to yield **6a**, 1) electron transfers are facilitated by the ease of oxidation of the Cu^I atoms, and 2)

⁶) The mechanisms of other electron-transfer reactions of *Grignard* reagents are reviewed in [27].

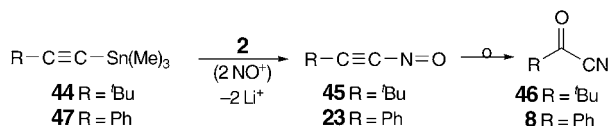
⁷) Studies of the mechanisms of coupling of copper acetylides by oxygen and by Cu^{II} reagents are reviewed in [4]; see also refs. cit. therein.

coupling or/and addition reactions of uncaged (discrete) phenylacetylenyl radicals (**14a**, R = Ph) are not extensively involved⁴).



Study has been initiated of the behaviors of highly covalent metal acetylides **1** with **2**. (*tert*-Butyl)(trimethylstannyl)acetylene (**44**) and **2** in Et₂O at –60° are reported to yield (*tert*-butyl)(nitroso)acetylene (**45**; *Scheme 9*; 40%) [3c]; other products were not identified. On storage in Et₂O at –30°, **45** is converted (*Scheme 9*) to trimethylacetyl cyanide (**46**; 30%) [3c] presumably by reactions similar to those in *Scheme 4*. Phenyl(trimethylstannyl)acetylene (**47**) and **2** in Et₂O at –60° are now found to give benzoyl cyanide (**8**; *Scheme 9*; 76–100%) apparently upon generation of nitrosoacetylene **23** and rearrangement *via* dimerization as in *Scheme 4*. Efficient generation and then reactions of 1-nitrosoacetylenes (**5**) at low temperatures offer excellent opportunities for developing their chemistries.

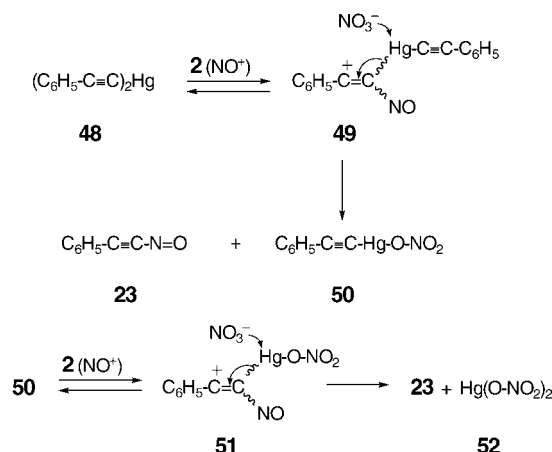
Scheme 9



Of further interest is that bis(phenylacetylenyl)mercury (**48**) and **2** in Et₂O at –78° (*Scheme 10*) yield benzoyl cyanide (**8**; >99%) efficiently. Nitroso(phenyl)acetylene (**23**) is apparently formed from mercuric acetylides **48** and **50** with **2** by directed nitrosative additions (NO⁺) and eliminations of mercuric derivatives **50** and **52** (*Scheme 10*), respectively. Dimerization of **23** and collapse as in **25** in *Scheme 4* then yield cyanide **8**. It is now clear that reactions of **2** with a metal acetylide (**1**) are greatly affected by the coordinated metal ion.

Conclusions. – Dinitrogen tetroxide (**2**) may react with metallo acetylides (**1**) in Et₂O and in hydrocarbon solvents at –78° to yield 1) conjugated diacetylenes **6** by oxidative processes in cage, 2) monoacetylenes **7** by H-abstraction reactions of the acetylen-1-yl free radicals (**15**) eventually generated, and/or 3) acyl cyanides (RCOCN) by rearrangements *via* dimerization of the 1-nitrosoacetylenes (**5**) initially formed. Which of the above reactions is dominant depends greatly on the metal of the metallo acetylides (**1**), the solvent, and temperature. Benzonitrile (**9**), a further product from metallo phenylacetylides (**1a** and **1f–1i**) and **2**, is presumed to be obtained from phenylacetylenyl nitrite (**26**) and then (or) nitroso(phenyl)ketene (**27**), followed by hydration and then decarboxylation and loss of H₂O. Phenylacetylene (**7a**) and **2** yield (*E*)- and (*Z*)-1,2-dinitrostyrenes (**34** and **35**, resp.), and 3-benzoyl-5-phenylisoxazole (**10**); **10** arises from cycloaddition of benzoyl nitrile oxide (**40**) to **7a**. The above results are of mechanistic interest in that the behaviors of various metallo acetylide radical cations (R–C⁺=C–M) are possibly revealed.

Scheme 10



Studies are to be made of 1) reactions of metal acetylides **1** with nitronium and other possible nitrating agents⁸), 2) syntheses and the properties of acetylen-1-yl nitrites (**4**), acetylen-1-yl nitrates ($\text{R}-\text{C}\equiv\text{C}-\text{O}-\text{NO}_2$), nitroketenes ($\text{R}(\text{O}_2\text{N})\text{C}=\text{C}=\text{O}$), and dinitroacetylene ($\text{O}_2\text{N}-\text{C}\equiv\text{C}-\text{NO}_2$), 3) efficient low-temperature methods for preparing 1-nitrosoacetylenes (**5**), and their conversions to 1-nitroacetylenes (**3**) and other valuable products, and 4) the chemistries of metallo radical cations as generated by coordination of various alkyl, vinyl, acetylenyl, aryl, heteroaryl, and non-carbon free radicals with Li^+ and other positive metal ions.

Experimental Part

General. Reaction solvents were dried and purified scrupulously prior to use. Et_2O and THF were distilled from Na or Na/K alloy with benzophenone as an indicator. Benzene and MeCN were each distilled from CaH_2 . CH_2Cl_2 , CHCl_3 , and CCl_4 were each distilled from P_2O_5 . Reaction mixtures were usually analyzed cold, rapidly, and directly by GC/MS/IR. Relative amounts of the components of a reaction mixture were determined by integration of peak areas in total ion chromatography as obtained mass spectrally. Quantitative measurements of yields were made by comparisons of peak areas to that of an internal standard (diphenylacetylene unless noted otherwise) in calibrated equipment. Melting points below 200° were determined in capillary tubes; those above 200° were obtained using glass plates. All melting points are uncorrected. NMR Spectra (peaks reported in ppm downfield from TMS at δ 0.00) were determined at 200.133 MHz for ^1H and 50.323 MHz for ^{13}C . High-resolution mass spectra (HR-MS) were obtained from The Ohio State University Chemical Instrument Center.

*Preparation of Solns. of N_2O_4 (**2**) in Et_2O .* Commercial **2** from a steel cylinder was condensed through Tygon tubing into a flask equipped for distillation and cooled to 0° . Compound **2** was then distilled into tared receivers cooled to 0° . The distillations removed plasticizers leached from the Tygon tubing. The receivers were removed and weighed. A measured volume of dry Et_2O cooled to 0° was added to **2**. Dry O_2 was bubbled through the cold solns. until the mixtures became amber. The solns. were kept at -25° and treated with dry O_2 before use. Solns. of **2** were replaced after 1 week or sooner.

*Lithium Phenylacetylide (**1a**) and **2**.* a) *Direct Addition.* BuLi (3.7 ml, 1.31M) in hexanes and then **2** (1.72 ml, 2.84M in Et_2O) were added by syringe dropwise into a soln. of phenylacetylene (**7a**; 0.5 g, 4.9 mmol) in Et_2O

⁸) Dinitrogen pentoxide (N_2O_5) converts **1k** in CCl_4 at -15° to diyne **6a** (55–78%) along with acetophenone (5%).

(10 ml) at -78° . A suspension formed immediately. Rapid analyses of the cold mixture by GC/MS/IR revealed that *diphenylbutadiyne* (**6a**; 80%) and **7a** (15%) were present. Upon warming to r.t., the mixture was poured into cold 5% aq. Na_2CO_3 and extracted rapidly with Et_2O . The Et_2O extracts were combined, dried (MgSO_4), filtered, concentrated *in vacuo*, and chromatographed (silica gel; hexanes/ AcOEt 4:1) to give **6a** (0.27 g, 55%) as slightly yellow crystals. Recrystallization from $\text{EtOH}/\text{H}_2\text{O}$ yielded **6a**, white needles, m.p. $85-87^{\circ}$ ([31]: $86-87^{\circ}$), whose FT-IR (NaCl, melt) and $^1\text{H-NMR}$ (CDCl_3) (δ 7.55–7.49 (m, 2 H); 7.31–7.35 (m, 3 H)) correspond to those of an authentic sample [31]. The aq. layer gave an instant positive test (blue color) for nitrite ion upon acidification with 5% aq. H_3PO_4 and application to KI/starch paper [32]. There was no evidence for production of *nitro(phenyl)acetylene* (**3**, R = Ph) in many such experiments.

b) *Inverse Addition*. An Et_2O soln. of **1a** (prepared from **7a** (0.50 g, 4.9 mmol) and BuLi (3.74 ml, 1.31M in hexanes)) was added by cannula (ca. 10 min) to **2** (1.72 ml, 2.85M in Et_2O) at -78° under Ar. Upon warming the mixture to r.t., addition of diphenylacetylene as an internal standard, and direct analysis by GC/MS/IR, **7a** (60%) and **6a** (13%) were found as reaction products. Compound **3** (R = Ph) was not detected.

Lithium Phenylacetylide (1a) and Excess 2. A mixture of BuLi (0.86 ml, 2.27M in hexanes) and **1a** (0.20 g, 1.96 mmol) in Et_2O (10 ml) at 0° was added by cannula in 50 min to a freshly prepared soln. of **2** (6.6 ml, 2.99M) in Et_2O at -78° . Direct analysis by GC/MS/IR showed **6a** (0.0487 g, 25%), *benzoyl cyanide* (**8**; 0.0123 g, 5%) [**6a**], *benzonitrile* (**9**; 0.0049 g, 2–3%) [**6b**] and *3-benzoyl-5-phenylisoxazole* (**10**; 0.0373 g, 15%) [**6c**] to be present. Diyne **6a** and isoxazole **10** (yellow crystals) were isolated by column chromatography (CC, silica gel; hexanes/ AcOEt 4:1). Anal. samples of **10** were obtained by recrystallization from hexanes or $\text{EtOH}/\text{H}_2\text{O}$. M.p. $81-82^{\circ}$ ([6c,d]: 89°). $^1\text{H-NMR}$ (CDCl_3): 8.3 (m, 2 H); 7.8 (m, 2 H); 7.5 (m, 6 H); 7.0 (s, 1 H). $^{13}\text{C-NMR}$ (CDCl_3): 185.8; 170.8; 162.4; 135.8; 134.1; 130.7; 130.7; 129.2; 128.6; 126.7; 126.0; 100.2. HR-MS: 249.0792 (M^+ ; calc. 249.0790), 105, 77, 51. Anal. calc. for $\text{C}_{16}\text{H}_{11}\text{NO}_2$: C 77.10, H 4.45; found: C 76.99, H 4.50.

Products **6a**, **8**, and **9** were identified by IR, MS, and GC retention times as compared to that from authentic samples.

Lithium Phenylethynolate (29) [17] and NOCl. BuLi (0.32 ml of a 2.27M soln. in hexanes) was added to a soln. of hexamethyldisilazane (0.128 g, 0.79 mmol) in THF (3 ml) at -78° . After 5 min, 1,1-dibromoacetophenone [**17**] (0.20 g) in THF (2 ml) was added dropwise. The mixture was brought to 0° , cooled to -78° , and *t*-BuLi (2.0 ml of a 1.1M soln. in hexanes) was added slowly. The mixture was stirred 15 min at -78° , and a freshly prepared soln. of NOCl in Et_2O (0.22 ml, 3.33M) was added. After 1 h, the mixture was warmed to 25° and the reaction was quenched rapidly with cold 10% aq. HCl. The org. layer was analyzed quickly by GC/MS/IR. The complex mixture contained **9** [**6b**] as the main constituent. *Phenylacetylenyl nitrite (26)* was not detected.

(Phenylacetylenyl)(phenyl)iodonium Toluene-4-sulfonate (30) [18] and NaNO_2 . A soln. of NaNO_2 (0.43 g, 6.3 mmol) in H_2O (10 ml) was added in one portion to **30** [**18a**] (0.30 g, 0.63 mmol) in CHCl_3 (10 ml), and the two-phase mixture was stirred vigorously for 3 d. TLC revealed the presence of 2 major products that GC/MS/IR showed to be *iodobenzene* (**32**, 81%) and **9** (45%). There was no evidence for **26**. CC (silica gel; hexanes/ AcOEt 4:1) of the product mixture led to separation of **32** and **9** (>45%), which were identified by comparisons with authentic samples.

Data of 9: FT-IR (gas phase): 3083w, 2235m, 1492m, 738s, 889s, 543s. MS: 103, 75, 50.

Sodium Phenylacetylide (1f) and 2. N_2O_4 (**2**, 11.4 ml, 1.72M in Et_2O , 19.6 mmol) was added at -78° to a stirred white suspension of **1f** prepared by agitation of Na (0.24 g, 10.3 mmol) with **7a** (1.00 g, 9.8 mmol) in Et_2O (40 ml) under Ar for 12 h. Reaction occurred rapidly. After slowly warming to r.t., the bright yellow suspension was poured into sat. aq. NaHCO_3 soln. and extracted with Et_2O . The Et_2O extracts were combined, dried (MgSO_4), concentrated, and chromatographed (silica gel; gradient elution with hexanes/ AcOEt) to give **7a** (0.16 g, 16%), **6a** (traces), **10** (0.28 g, 23%, yellow needles, m.p. $80-81.5^{\circ}$; [**6c-d**]: 89° , MS: 249 (M^+), 105, 77, 51), and (*E*)- and (*Z*)-1,2-dinitrostyrenes (**34** and **35**, resp., are major products) [20a], assigned by FT-IR and comparison with authentic samples, resp.

Phenylacetylenylmagnesium Bromide (1g) and 2. EtMgBr was prepared by adding 1,2-dibromoethane (1 drop) to a suspension of EtBr (0.216 g, 1.98 mmol), Mg turnings (0.095 g, 3.90 mmol), and anh. Et_2O (2 ml). The Et_2O soln. was added *via* cannula to **7a** (0.20 g, 2.00 mmol) in Et_2O at r.t. After stirring for 20 min, the mixture was cooled to -78° and THF (2 ml) was added to dissolve the solids completely. Purified **2** (0.82 ml of a 2.38M solution in Et_2O) was added dropwise. Analysis of the mixture by GC/MS/IR revealed that the major product was **7a** (>60%); **6a** (20%), (*Z*)- and (*E*)-1,2-dibromostyrenes, and **8** (trace) were also present. (The 1,2-dibromostyrenes were formed by reaction of **7a** with Br_2 as produced by oxidation of Br^- with **2**.) No **3** (R = Ph) was found in the reaction product.

Phenylacetylenylzinc Chloride (1h), Phenylacetylenylzinc Bromide (1i), and Phenylacetylenylzinc Iodide (1j), Respectively, with 2. Solns. of BuLi (1.7 ml, 1.18M in hexanes) and then anh. ZnCl_2 (0.28 g, 2.0 mmol) in

THF (3 ml) were added to **1a** (0.20 g, 2.00 mmol) in THF (5 ml) at -78° under Ar. The mixture was rapidly warmed to r.t. and then cooled to -78° . After dropwise addition of **2** (0.82 ml, 2.4M in Et₂O) and warming the mixture to r.t., direct GC/MS/IR analysis revealed **7a** as a major component. The mixture was poured into 5% Na₂CO₃, washed with brine, and concentrated *in vacuo* to a yellow liquid (0.19 g), which was separated by CC (silica gel; 3% AcOEt in hexanes) to give **6a** (0.04 g, 20%) and **7a** (0.15 g, 76%).

In an experiment similar to that with **1a**, BuLi, and ZnBr₂ and then **2** at -78° , the reaction products from **1i** are **6a** (20%) and **7a** (76%). From **1a**, BuLi, ZnI₂, and then **2** at -78° , **6a** (17%) and iodo(phenyl)acetylene (74%) are obtained. Iodo(phenyl)acetylene was identified by comparison with an authentic sample.

Copper Phenylacetylide (1k) and 2. An Et₂O soln. of **2** (1.5 ml, 1.24M, 1.8 mmol) was added dropwise to a stirred suspension of **1k** (0.30 g, 1.8 mmol) [27] in dry Et₂O (10 ml) at -78° under Ar. Reaction began almost immediately, and the suspension changed from yellow to dark green. The heterogeneous mixture was slowly warmed to r.t., filtered through *Celite*, washed rapidly with 5% aq. Na₂CO₃ and brine, dried (MgSO₄), and concentrated. Nitroacetylene **3** (R = Ph) and **7a** were not reaction products. After the concentrate had been dried at 1 mm Hg, diacetylene **6a** (0.13 g, 72%) remained as yellow crystals, m.p. 75–81°. The crude **6a** (0.11 g, 61%) was chromatographed (silica gel; hexanes/AcOEt 4:1) and then recrystallized from EtOH/H₂O. White crystals of **6a** (0.09 g, 50%) were obtained: m.p. 85–87° ([31]: 86–87°).

In a similar experiment in which **1k** was added (50 min) to excess **2** at -78° , **6a** was formed in 60% yield. The crude reaction product did not contain **3** (R = Ph) or **7a**.

Dilithium Tris(phenylacetylenyl) Cuprate (1l) and 2. To **7a** (0.20 g, 2.0 mmol) in Et₂O (10 ml) was added BuLi (0.86 ml, 2.27M in hexanes) at -78° and **1k** (0.16 g, 1.0 mmol) [28]. The mixture warmed to r.t. overnight. The bright yellow color of **1k** had disappeared, and the soln. was almost completely homogeneous. The mixture was cooled to -78° , and **2** (0.57 ml, 1.73M in hexanes) was added. The soln. became dark immediately and contained a yellow suspension. After 10 min, the cold mixture was filtered through *Celite* and washed thoroughly with CH₂Cl₂. The filtrate was dried (K₂CO₃) and concentrated to **6a** (0.14 g, 71%), a yellow solid, which, on recrystallization from EtOH/H₂O, gave colorless needles (0.10 g, m.p. 83.5–85°), identical with an authentic sample of **6a** [31].

Lithium Pent-1-ynide (1b) and 2. Pent-1-yne (**7b**, 0.50 g, 7.4 mmol) in Et₂O (10 ml) was cooled under Ar to -78° . BuLi (5.6 ml, 1.31M in hexanes, 7.4 mmol) and then **2** (2.6 ml, 2.85M in Et₂O, 7.4 mmol) were added. After stirring the mixture at -78° for 10 min, chloro(trimethyl)silane (1 ml) was added to quench any remaining **1b**. The soln. was warmed to r.t. in 1 h, poured into 5% aq. Na₂CO₃ soln. (50 ml), and extracted with Et₂O. The extracts were combined, dried (MgSO₄), and analyzed by GC/MS/IR for *deca-4,6-diyne* (**6b**, 0.15 g, 30%) [33]. The extract was treated with AgNO₃ in EtOH/H₂O to convert **7b** to silver pent-1-ynide (white). The white precipitate, after filtration, washing with H₂O, EtOH, and Et₂O, and drying weighed 0.73 g, which corresponded to 0.28 g of **7b** (57%). Diyne **6b** was isolated by prep. GLC. ¹H-NMR (200 MHz, CDCl₃): 2.20 (*t*, *J* = 7, 4 H); 1.52 (*q*, *J* = 7, 4 H); 0.96 (*t*, *J* = 7, 6 H). MS: 134, 117, 105, 91, 77, 63, 51, 32. The spectra of **6b** are identical with those reported in [33].

Lithium (Trimethylsilyl)acetylide (1c) and 2. A soln. of **1c** (0.20 g, 2.0 mmol) in Et₂O (10 ml) was flushed with Ar and cooled to -78° . BuLi (0.90 ml, 2.27M in hexanes, 2.0 mmol) was added, followed by **2** (1.6 ml, 1.24M in Et₂O, 2.0 mmol). The soln. was stirred for 1 h at -78° and then poured into 5% aq. Na₂CO₃ soln. The org. layer was distilled to remove the **7c** and Et₂O. The distillate was treated with AgNO₃ in EtOH/H₂O to convert the **7c** to disilver acetylide (AgC≡CAg), which, when filtered, was washed with H₂O, EtOH, and Et₂O, and dried, weighed 0.12 g, and corresponded to 0.05 g of the initial **7c** (25%). Prep. GLC of the initial distillation residue led to isolation of *bis(trimethylsilyl)butadiyne* (**6c**; 44%) [34]. FT-IR (gas phase): 2967w, 2907w, 2064m, 1261w, 850s, 648w. ¹H-NMR (200 MHz, CDCl₃): 0.16 (*s*, 18 H). MS: 194 (*M*⁺), 179, 163, 149, 121, 97, 73, 67, 32. The spectra of **6c** are identical with those reported in [34].

Lithium (Phenylsulfonyl)acetylide (1d) and 2. To a soln. of (*phenylsulfonyl*)acetylene (**7d**; 0.20 g, 1.2 mmol) in Et₂O (10 ml) at -78° under Ar was added BuLi (0.5 ml, 2.27M in hexanes, 1.1 mmol). A cold soln. of **2** (5.7 ml, 0.21M in Et₂O) was then added dropwise. The cooling bath was removed, and the mixture was warmed slowly to ca. 20°. After addition of aq. HCl (10%), the org. layer was separated, dried, and concentrated to give **7d** (95%) as identified by its IR and ¹H-NMR spectra.

Bis(phenylacetylenyl)mercury (48) and 2. A soln. of **2** (0.32 ml, 3.13M) in Et₂O was added dropwise to **48** (0.20 g, 0.50 mmol) in Et₂O (10 ml) and stirred at -78° under Ar. A white precipitate formed immediately. After warming to r.t. (ca. 0.5 h), the heterogeneous mixture became yellow. The mixture was filtered rapidly through silica gel and concentrated under reduced pressure. The yellow residue (0.13 g) was analyzed by GC/MS/IR and found to be essentially totally **8** (> 99% yield) [6a]. FT-IR (gas phase): 3080w, 2218, 1700 (C=O),

1598, 1451, 1244, 1180, 980, 699. MS: 131 (M^+), 105 ($[M - CN]^+$), 77, 51. The spectra of the product are identical with those of an authentic sample of **8** [6a].

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