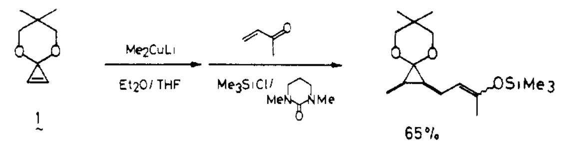
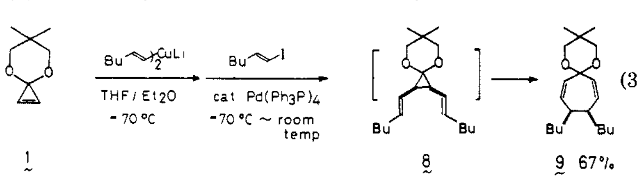
cyclopropane **2** much faster than alkyl iodides (without HMPA, -70 °C, 10 min) to give cis-allylated product **3d** in 81% yield (entry 3). Cuprates with nontransferrable "dummy" ligands, e.g., silylethynyl[6] (entries 4 and 9) and phenylthio[7] (entry 5) ligands, underwent smooth addition, and the resulting copper species cleanly reacted with 1 equiv of electrophiles (entries 4 and 5). The Me_3SiCl-accelerated conjugate addition[8] of the cuprio cyclopropane also proceeded in good yield (eq 2).



(2)

Thermal rearrangement of the vinylcyclopropanone ketals, prepared by addition of vinyl cuprates, proceeded with great facility due to the accelerating effect[9] of the ketal moiety (Scheme II). Thus, heating of the cyclopropanes **4–6** at 240–290 °C in toluene resulted in the formation of substituted 3-cyclopentenone ketals in 50–80% yield. The rearrangement proceeded with exclusive migration of the electronically favored ketal carbon (Scheme II, path a) rather than the sterically favored methylene carbon (path b). The net carbocupration rearrangement provides a powerful [3 + 2] annulation method. The rearrangement of **7** illustrates the utility of the reaction sequence for attachment of a five-membered ring to an existing ring system.

The stereoselective formation of cis-disubstituted cyclopropanes led to the development of a novel *single-pot* assembly of seven-membered rings in a [3 + 2 + 2] fashion via divinylcyclopropane[10] (**8**). Namely, addition of *trans*-hexenyl cuprate (1.1 equiv)



(3)

followed by trapping of the intermediate with *trans*-hexenyl iodide (3.0 equiv) *in the presence of Pd(0)*[11] at -70 to 25 °C (5 h) directly afforded the 4,5-*cis*-dibutylcycloheptadienone ketal **9** in 67% yield.[12] The formation of the cis isomer **9** is due to the boat transition state in the rearrangement of **8**.[10]

Works to explore the generality of the carbometalation reaction of cyclopropenes as well as the utility of the cyclopropanone ketals in homoenolate chemistry[13] are in progress.[14]

Supplementary Material Available: Physical data for **3a,c,d** and other new compounds (6 pages). Ordering information is given on any current masthead page.

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(11) Substitution reaction of the vinyl iodide did not proceed in the absence of $Pd(Ph_3P)_4$.

(12) The ^{13}C NMR spectrum revealed the C_s symmetry of the product, which in turn supported the expected cis dibutyl structure.

(13) Cf. Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *108*, 3745.

(14) Typical procedure: cuparate addition/MVK trapping (eq 2). To a solution of Me_2CuLi (2.2 mmol) in a 2:3 ether/THF mixture (5 mL) at -70 °C was added during 30 s a solution of the cyclopropene **1** (2.0 mmol). After 1 min were added sequentially THF solutions of *N,N*-dimethylpropylene urea (5 mmol), Me_3SiCl (5 mmol), and methyl vinyl ketone (4.4 mmol). After 2 h at -70 to -30 °C, triethylamine (6 mmol) and hexane (6 mL) were added. Workup as reported (ref 6a) followed by silica gel chromatography gave the conjugate adduct as enol silyl ether (387 mg, 65%).

Generation and Trapping of an Alkynyl Cation

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Disubstituted cations, vinyl and phenyl cations, are accepted organic intermediates.[1] They have been generated, e.g., by solvolytic processes, and some stabilized vinyl cations have even been observed by ^1H and ^{13}C NMR spectroscopy under non-nucleophilic conditions.[2] We report here for the first time on the generation in solution of the alkynyl cation **1**, which has been previously observed only in mass spectrometry.[3]

Satisfactory agreement exists between the calculated and the experimental value (ca. 390 kcal mol^{-1}) of the heat of formation of the alkynyl ion **1** (R = H).[4] Accordingly, ion **1** (R = H) is ca. 130 kcal mol^{-1} less stable than a methyl cation and ca. 120 kcal mol^{-1} less stable than a primary vinyl and phenyl cation.[1] Owing to its exceedingly low stability, solvolytic procedures to generate an alkynyl cation **1** met with no success,[5] even by resorting to very good leaving groups, i.e., N_2, as in the decomposition of alkynyldiazonium salts **2** (R = C_6H_5, p-ClC_6H_4; X^- = $SbCl_5Ts^-$).[6] This is explained by recent ab initio calculations,[7]

$$\underset{\mathbf{1}}{R-C\equiv C^{\oplus}} \qquad \underset{\mathbf{2}}{R-C\equiv C-\overset{\oplus}{N}\equiv N \quad X^{\ominus}}$$

showing that the dissociation energy of the alkynyl diazonium ion **2** (R = H) to form a singlet alkynyl cation **1** (R = H) and an N_2 molecule amounts to ~150 kcal mol^{-1}. Even considering that the energy of a singlet alkynyl cation **1** (R = H) lies between 64 and 69 kcal mol^{-1} above that of the triplet ground state,[4,7] one must conclude that dediazonation of an alkynyl diazonium ion **2** under solvolytic conditions is hardly a suitable procedure to generate an alkynyl cation **1**.

Spontaneous nuclear decay of a tritium atom in a tritiated organic molecule represents a well-established method to generate highly unstable carbocations of defined structure under all experimental conditions (Scheme I).[8] By this method, both singlet primary vinyl and aryl cations were readily generated from multitritiated ethylene[9] and arenes,[10] respectively under conditions

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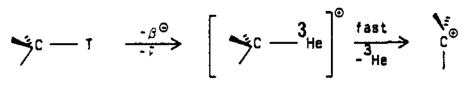
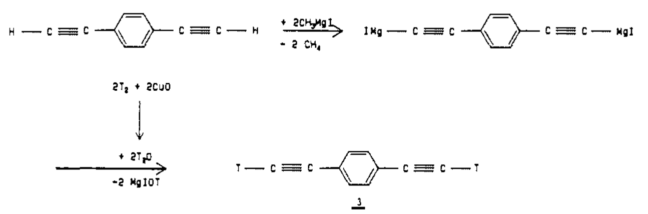
Scheme I

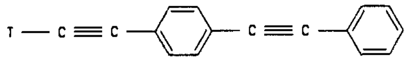


Scheme II

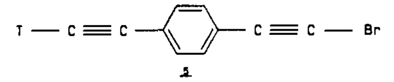


allowing investigation of their reactivity in the gaseous and condensed phase. This nuclear decay procedure has been extended to the generation of the alkynyl cation **1**. Thus 1,4-bis(tritioethynyl)benzene (**3**) was synthesized according to the reaction sequence given in Scheme II.[11] The synthesis was carried out in very dry sealed reaction vessels. The product from blank deuteriation experiments has been examined by MS and ^{1}H NMR analyses. 1,4-Bis(deuterioethynyl)benzene was formed in these blank runs in over 90% yield. Radio HPLC and GC of the tritiated reaction mixture showed the exclusive formation of **3** in comparable yields.[12] The mixture, extracted with inactive benzene, was subjected to azeotropic distillation to remove residual tritiated water. Samples of the purified solution corresponding to ca. 1 mCi (18.7 Ci mol^{-1}) of **3** were introduced into Pyrex ampoules containing variable amounts of liquid or gaseous nucleophiles. After sealing they were stored in the dark for ca. 6 months at room temperature. To avoid selective loss of the acidic tritium atoms of **3** by prototropic exchange with the nucleophile during the storage period, only aprotic nucleophiles (benzene, 1,4-dibromobutane, *tert*-butyl bromide) were employed to trap the ionic species arising from the nuclear decay of **3**.

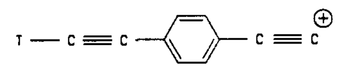
By using authentic samples for comparison, radiochromatographic analysis of the decayed mixtures revealed the formation of significant yields of **4** (96%) from liquid benzene (0.3 mmol) and of **5** (36 and 31%) from liquid 1,4-dibromobutane (8.3 mmol) and *tert*-butyl bromide (8.9 mmol), respectively. The absolute yield of **5** decreased to 7% and 9% in gaseous *tert*-butyl bromide at 10 (0.26 mmol) and 50 Torr (1.33 mmol), respectively. Most of the residual activity recovered in the mixture containing brominated nucleophiles is due to polybrominated products, which are under investigation. Formation of the tritiated products is not accompanied by any detectable amounts of the corresponding unlabeled forms (<10^{-5} mol%). This excludes any other conceivable (thermal, photochemical, radiolytic, etc.) source for the radioactive products **4** and **5**.



4



5



6

Isolation of tritiated products **4** and **5** from the corresponding decay mixtures could point to the actual occurrence of the tritiated alkynyl cation **6** from spontaneous nuclear decay in **3** and its subsequent trapping with a nucleophile.

The same products may well arise from displacement of the ^{3}He in the primary daughter ion $[TC{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}^3He]^+$ by the nucleophile. In fact, at variance with the repulsive nature of most common C–He bonds,[13] the C–He dissociation in $[H{-}C{\equiv}C{-}He]^+$ has been calculated to range about 1 eV.[14] However, this energy can be readily provided by the recoil energy (maximum value of several eV) imparted to the ^{3}He moiety by the leaving β^- and $\bar{\nu}$ particles after the decay event,[15] so that a significant fraction of the primary species $[R{-}C{\equiv}C{-}^3He]^+$ is expected to dissociate rapidly to **1** before interacting with the nucleophile.

The present results provide first evidence on the transient existence of an alkynyl cation, such as **6**, in both gas phase and solution and on its behavior toward several organic molecules. The exceptional leaving group ability of the ^{3}He atom in $[R{-}C{\equiv}C{-}^3He]^+$, formed from β^- decay of $R{-}C{\equiv}C{-}T$, allows unimolecular cleavage of the C–^{3}He bond, and, therefore, formation of **1** becomes energetically accessible.

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[12] HPLC: 15-cm 5-micron Alltech Rosil C-18 column from Alltech, Italy, using a 65:35 MeOH/H_2O solvent system (0.5 mL min^{-1}), connected to a Berthold LB 503 HS flow scintillation counter; GC: 2-m $^1/_8$ in. 10% SP2100 on 100–120 mesh Supelcoport at 100 °C, connected to a Berthold proportional counter tube kept at 120 °C.

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A Rigid and Nonperturbing Probe for Duplex DNA Motion

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The structural heterogeneity of duplex DNA and its complexes with proteins suggests that not only is the *conformation* of a sequence of bases in DNA critical to normal function but also the *dynamics* of certain sequences may be important.[1] While progress has been made in the study of DNA local dynamics, experimental studies[2] of particular base sequences (other than homopolymers) have to date been prevented by the lack of a technique which focuses on a specific location in a given sequence. Electron paramagnetic resonance (EPR) spectroscopy should be well suited to detecting sequence dependent DNA dynamics[3-5] but requires a method for the site-specific introduction of a paramagnetic probe. Such studies are further complicated by the

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