The title compounds were shown to be useful as alkene substrates in the arylthio-mediated one-pot multi-component coupling leading to the formation of functionalised alkylidenes.

Multi-step sequential transformations are widely used in organic synthesis. Among organic reactions employed as basic steps in these sequences, very few belong to the category of AdE processes and those are nearly exclusively intramolecular. Previously, we suggested a novel protocol for the one-pot multi-component coupling based upon the arylthio-mediated controlled sequence of the intermolecular AdE reactions, which proceed via the formation of bridged sulfonium ion species as stable intermediates. This approach was successfully applied to a number of three- and four-component couplings outlined in Scheme 1.

Initially we investigated an opportunity to use DCHC complexes of other conjugated components coupling (option A, Scheme 1). It was found that DCHC complex of isopropenyl acetylene reacted readily with p-tolyl sulfenyl chloride to give corresponding 1,2-adduct. The in situ formation of the latter species to serve as efficient electrophiles in the reactions with π-donors such as 1-phenyl-1-(trimethylsiloxy)ethylene, methyl trimethylsilyl dimethylketene acetal, 2-trimethylsiloxyfurane, 1-(trimethylsiloxy)cyclopentene and 1-cyclopropyl-1-(trimethylsiloxy)ethylene followed by the decomplexation furnished adducts 12–16 (Scheme 2).†,‡,§

The sequence of reactions shown in Scheme 2 was found to work equally well with DCHC complexes of other conjugated enynes such as 17–19 and resulted in the formation of expected products 20–23 in satisfactory to good yields (Scheme 3).†

The above data clearly indicated that the presence of the β-arylthio group as an additional cation-stabilising moiety in DCHC complexed propargyl cation intermediates 3a–d did not affect noticeably the ability of the latter species to serve as efficient electrophiles in the reactions with π-donors and hence yields (not optimised) refer to the isolated and purified products. The structures were unambiguously established by 1H and 13C NMR spectra and HRMS and/or satisfactory elemental analysis. Adducts 14 and 15 were formed as a mixture of diastereomers in ratios of 1:1 and 2.5:1, respectively.

Typical experimental procedure. To a stirred solution of DCHC complex of isopropenyl acetylene (0.352 g, 1 mmol) in CH2Cl2 (20 ml) at –70 °C a solution of p-TolSCI (0.159 g, 1 mmol) in CH2Cl2 (1 ml) was added, followed by TiCl4 (0.11 ml, 1 mmol). After 30 min, the TLC data revealed the complete disappearance of starting compound 1. Then, the temperature was raised up to –45 °C and methyl trimethylsilyl dimethylketene acetal (0.328 g, 2 mmol) was added. The mixture was kept at this temperature for 30 min and quenched with NaHCO3. An usual workup followed by column chromatography gave DCHC complex of 2,2,3-trimethyl-3-p-tolylsulfenylmethylpent-4-ynoic acid methyl ester as a deep-red oil, which was dissolved in acetone (15 ml) and treated with cerium(IV) ammonium nitrate (3 mmol) at 0 °C for 15 min (TLC control). The solvent was removed on a rotary evaporator, the residue was dissolved in chloroform and washed with brine. After preparative TLC, adduct 13 was isolated as an individual compound in 75% yield. 1H NMR (300 MHz, CDCl3): δ: 1.41, 1.42 and 1.45 (3s, 9H), 2.28 (s, 1H), 2.35 (s, 3H), 3.1 and 3.47 (dd, 2H), 3.75 (s, 3H), 7.13 and 7.36 (dd, 4H). 13C NMR: δ: 20.9, 22.2, 22.3, 25.6, 43.0, 48.7, 51.8, 72.0, 86.3, 129.5, 130.0, 133.9, 136.0, 175.7. HRMS (Finnigan Mat 95): m/z: 291.1420 (M + H)+.

**Scheme 1**

\[
\begin{align*}
\text{Nu} &= \text{OH, OR, etc.}
\end{align*}
\]

\[
\begin{align*}
\text{MR} &= \text{X = O, CH2, M = Si, Sn}
\end{align*}
\]
the DCHC complexes of conjugated enynes could be used as alkene-I components in the sequences shown in Scheme 1.

In a related series of experiments, we have investigated the reactivity pattern of the DCHC complexed conjugated enynes as alkene-II substrates in the AdE reactions with ESI electrophiles generated

\[ \text{in situ} \] upon the interaction of \( \beta \)-arylthio-\( \alpha \)-chloroalkyl methyl ethers with Lewis acids (option B, Scheme 1).\(^4,5\) In a typical experiment, vinyl methyl ether \(24\) was first treated in a \( \text{CH}_2\text{Cl}_2 \) solution at \(-70^\circ\text{C}\) with 1 equivalent of \( p\)-TolSCl followed by 1 equivalent of \( \text{SnCl}_4\). The ESI-like intermediate \(25\) thus generated reacted readily with DCHC complex \(1\) at \(-60^\circ\text{C}\) (TLC control) to give the next stabilised cationoid intermediate tentatively identified as cyclic thiophanium ion (TPI) \(26\). Here again no attempts were made to isolate intermediate \(26\) as a stable salt, but the results of its quenching with standard nucleophiles fully corroborated with the expected reactivity pattern of the TPI-like intermediates (Scheme 4) (cf. refs. 3–7).

Thus, the treatment of intermediate \(26\) with a \( \text{MeOH–K}_2\text{CO}_3\) mixture produced (after oxidative decomplexation) methoxy adduct \(27\), while hydroxy adduct \(28\) was formed upon the quenching of \(26\) with \( \text{Bu}_4\text{NOH}\). Hydride reduction of \(26\) with \( \text{Bu}_4\text{NBH}_4\) resulted in the formation of adduct \(29\) contaminated by proton elimination adduct \(30\). The latter was formed as the sole product in the reaction of \(26\) with \( \text{Et}_3\text{N}\).

Under similar conditions, the interaction of ESI \(25\) with the DCHC complex of 1-ethynylcyclohexene \(31\) resulted in the generation of intermediate \(32\) as is evidenced by the formation of the corresponding products of proton elimination \(33a, b\) or hydride reduction \(34\) upon the treatment with \( \text{H}_2\text{O–NaHCO}_3\) or \( \text{Bu}_4\text{NBH}_4\), respectively (Scheme 5). It is noteworthy that in the latter case only one of the four possible diastereomers was isolated (NMR data, stereochemistry undetermined).

To summarise, the above data clearly indicated that the protocol elaborated earlier to carry out the tandem sequence corresponding to the general equation:

\[
\text{ArS + vinyl ether-I + vinyl ether-II + nucleophile} \rightarrow \text{adduct3–7}
\]

is also applicable to the transformations which involve the usage of the DCHC complexes of conjugated enynes instead of vinyl ethers as either one of the alkene components. Both options of the one-pot coupling described in this paper seem to be promising for the elaboration of a new route for a ready assembly of the polyfunctional adducts bearing a triple bond moiety from simple precursors.

Throughout this paper \([\text{Co}]\) refers to \( \text{Co}_2(\text{CO})_6\) and \( \text{Ar}\) refers to \( p\)-Tolyl.

**Scheme 2**

the DCHC complexes of conjugated enynes could be used as alkene-I components in the sequences shown in Scheme 1.

In a related series of experiments, we have investigated the reactivity pattern of the DCHC complexed conjugated enynes as alkene-II substrates in the AdE reactions with ESI electrophiles generated \textit{in situ} upon the interaction of \( \beta \)-arylthio-\( \alpha \)-chloroalkyl methyl ethers with Lewis acids (option B, Scheme 1).\(^4,5\) In a typical experiment, vinyl methyl ether \(24\) was first treated in a \( \text{CH}_2\text{Cl}_2 \) solution at \(-70^\circ\text{C}\) with 1 equivalent of \( p\)-TolSCl followed by 1 equivalent of \( \text{SnCl}_4\). The ESI-like intermediate \(25\) thus generated reacted readily with DCHC complex \(1\) at \(-60^\circ\text{C}\) (TLC control) to give the next stabilised cationoid intermediate tentatively identified as cyclic thiophanium ion (TPI) \(26\). Here again no attempts were made to isolate intermediate \(26\) as a stable salt, but the results of its quenching with standard nucleophiles fully corroborated with the expected reactivity pattern of the TPI-like intermediates (Scheme 4) (cf. refs. 3–7).

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