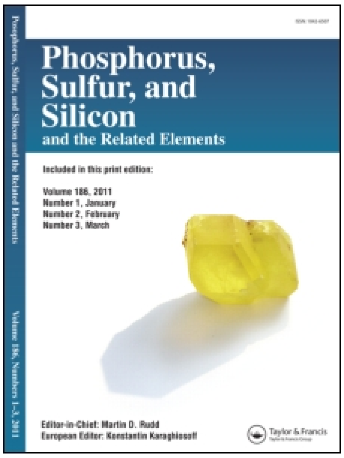


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ArS-Mediated Ad<b><i>E</i> Reaction of the Cobaltcarbonyl-Complexed Conjugated Enynes

Vasilii V. Tumanov[a]; William A. Smit[a]
[a] N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

To cite this Article Tumanov, Vasilii V. and Smit, William A.(2005) 'ArS-Mediated Ad<b><i>E</i> Reaction of the Cobaltcarbonyl-Complexed Conjugated Enynes', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 5, 1279 — 1283

To link to this Article: DOI: 10.1080/10426500590911584
URL: http://dx.doi.org/10.1080/10426500590911584

Phosphorus, Sulfur, and Silicon, 180:1279–1283, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590911584

Taylor & Francis
Taylor & Francis Group

ArS-Mediated Ad_E Reaction of the Cobaltcarbonyl-Complexed Conjugated Enynes

Vasilii V. Tumanov
William A. Smit
N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

A novel approach to the synthesis of functionalized enynes is elaborated based on the protocol of the three-component coupling of arenesulfenyl chlorides, dicobalthexacarbonyl complexes of the conjugated enynes, and nucleophiles of the π-donor type and a possibility to employ the 1,6-enyne derivatives thus prepared as the substrates for the intramolecular Pauson–Khand cyclization is demonstrated.

INTRODUCTION

Nicolas reaction[1] is one of the most effective and convenient methods for the preparation of various functionalized alkynes. A useful modification of this reaction involves the controlled two-step sequence of Ad_E reactions across the double bond of dicobalthexacarbonyl (DCHC) complexes of the conjugated enynes via an intermediacy of the cobalt-complexed propargylic cation.[2–4] However, the latter option is of a limited preparative usefulness for the substrates bearing an additional substituent at the propargylic center and in general its diastereoselectivity is rather low.

Here we present a new scheme of the modified Nicolas reaction based upon the use of arylsulfenium chlorides as the starting electrophiles in the aforementioned sequence. The presence of ArS moiety secures the formation of extra stabilized episulfonium-like intermediate. As a result a significant extention of the scope and improvement of the diastereoselectivity of the coupling is achieved.

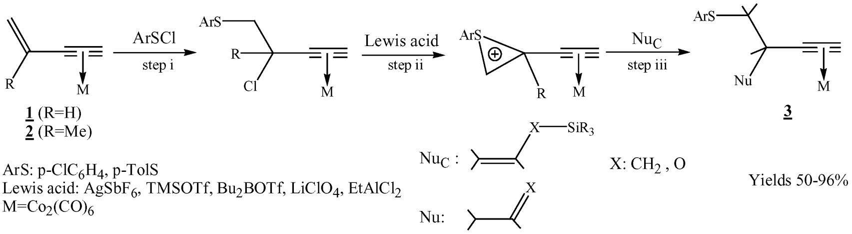
Received July 9, 2004; accepted October 5, 2004.

We are indebted to Deutsche Forschungsgemeinschaft (Grant No. MA673/19) and to RFBR (Grants Nos. 03-03-32884 and 03-03-04001) for financial support of this work.

Address correspondence to Vasilii V. Tumanov, N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Russian Federation, 119991 Moscow, Leninsky prosp. 47, Russia. E-mail: Vasilii_Tumanov@mail.ru

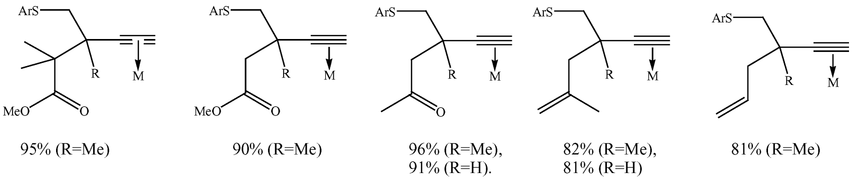
RESULTS

DCHC complexes of vinylacetylene **1** and isopropenylacetylene **2** were chosen as the model substrates in the reaction sequence shown in Scheme 1. p-Chlorobenzene and p-methylbenzene sulfenyl chlorides were used as a starting electrophiles at step (i). Various Lewis acids were shown to be efficient at step (ii). At the final step (iii), we used a set of the standard silyl-capped π-donors as carbon nucleophiles (Nu_C).



SCHEME 1

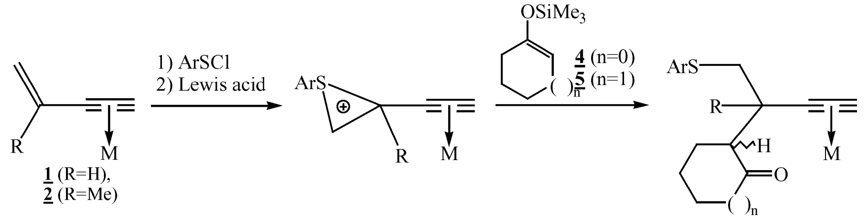
A list of the represented examples shown in Scheme 2 demonstrates a rather wide scope of the investigated reaction, which was found to be applicable to virtually all combinations of the substrates involved (in all these cases $EtAlCl_2$ was employed as Lewis acid).



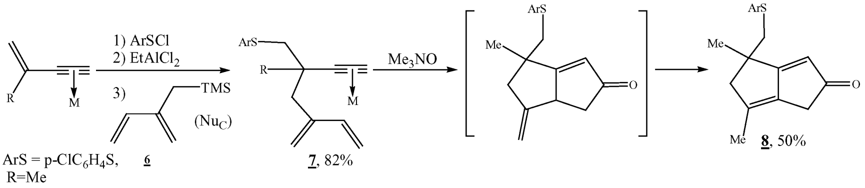
SCHEME 2

Classic Nicolas reaction and its analogues,[1–4] except for some particular cases,[5] exhibits a rather low diastereoselectivity of the overall coupling. We disclosed that β-arylthiosubstituted cobalt-complexed propargylic cation prepared from **1** reacts with prochiral 1-trimethylsilyloxycyclopentene **4** and 1-trimethylsilyloxycyclohexene **5** to give the corresponding adducts with good to excellent diastereoselectivity depending on the Lewis acid used (Scheme 3, Table I). As might have been expected, a substantially lower diastereoselectivity was observed for the coupling using enyne complex **2**.

The usefulness of the aforementioned sequence for the synthesis of the substrates directly amenable for the intramolecular Pauson–Khand (IMPK) reaction[6] cyclization is shown in Scheme 4. This option is based on the use of 2-(trimethylsilylmethyl)buta-1,3-diene **6**, as the final Nu_C



SCHEME 3



SCHEME 4

bearing an additional vinyl group. It was shown that the presence of the conjugated diene moiety in the silane **6** does not affect essentially the efficiency of the coupling and the respective product **7** was prepared in high yield.

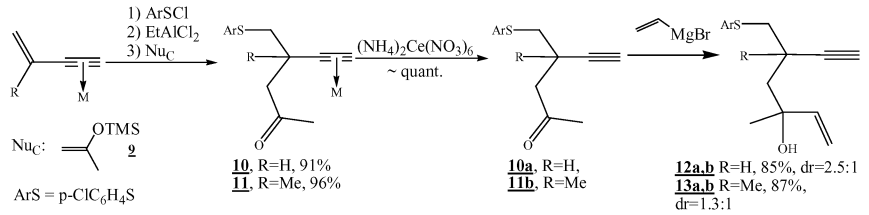
Ample literature data on the synthetic application of the IMPK cycloaddition[6] do not contain any reference to its applicability for the 1,6-enynes that contain alkene unit as the part of the conjugated diene

TABLE I

Substrate	Nu$_C$	Lewis acid	Ratio of diastereomers (*syn:anti*)	Yield (%)
1	**4**	AgSbF$_6$	20 : 1	52
1	**4**	TiCl$_4$	17 : 1	90
1	**4**	TMSOTf	12 : 1	56
1	**4**	Bu$_2$BOTf	10 : 1	61
1	**4**	EtAlCl$_2$	3 : 1	92
1	**5**	TiCl$_4$	12 : 1	87
1	**5**	EtAlCl$_2$	7 : 1	86
2	**4**	AgSbF$_6$	3.8 : 1	50
2	**4**	TiCl$_4$	3.5 : 1	91
2	**4**	TMSOTf	3.5 : 1	54
2	**4**	Bu$_2$BOTf	3.0 : 1	59
2	**4**	EtAlCl$_2$	2.5 : 1	91
2	**5**	TiCl$_4$	2.5 : 1	85
2	**5**	EtAlCl$_2$	2.2 : 1	82

system. We have found that this type of compound can serve as the suitable substrates for this reaction and the adduct **7** readily underwent the conversion into the respective bicyclo[3.3.0]octadienone **8** under the standard cyclization conditions.[7]

An alternative approach for the synthesis of the 1,6-enynes takes an advantage of an easy preparation of the DCHC complexes of 5-oxoalkynes as a result of the above described three components coupling with the use of silyl enol ethers as the C-nucleophiles. It was anticipated that these adducts could be further transformed into the required 1,6-enynes by the Grignard addition of vinylmagnesium bromide. To check the viability of this approach we have chosen DCHC complexes of oxoalkynes **10** and **11** prepared in virtually quantitative yields with the use of 2-trimethylsilyloxypropene (**9**) as Nu_C (see Scheme 5).

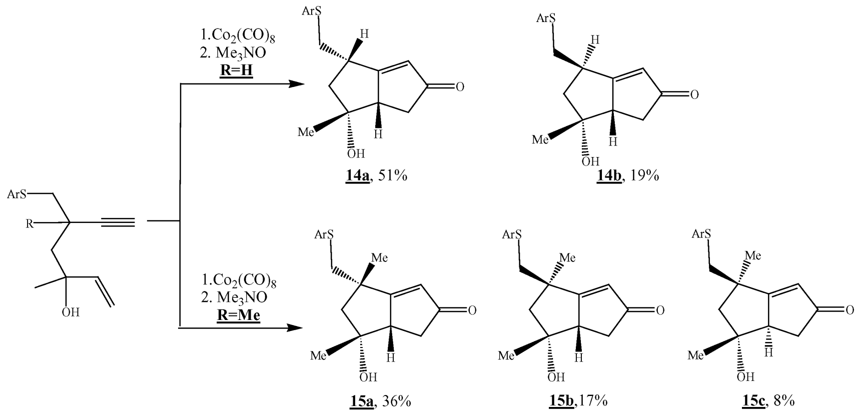


SCHEME 5

Unfortunately, the attempts to carry out the Grignard reaction of vinylmagnesium bromide directly with DCHC complexes **10** and **11** turned out to be rather unsuccessful. At the same time, we faced no problems when performing the reaction of vinyl magnesium bromide with the decomplexed adducts **10a** and **11a** and the respective 1,6-enynes **12a**,**b** and **13a**,**b** were prepared in good yields as mixtures of diastereomers.

The separation of diastereomers failed. Therefore, further transformations were performed with the mixtures of diastereomers **12a**,**b** and **13a**,**b**. The reaction of these adducts with $Co_2(CO)_8$ resulted in the formation of the respective DCHC complexes. The latter were not isolated but used directly as the substrates for the IMPK reaction under the conventional conditions of the oxidative initiation under the action of Me_3NO.

It was found that the cyclization of the mixture **12a**,**b** produced a mixture of only two (out of four possible) diastereomers **14a**,**b** in the ratio 2.5:1, which roughly corresponded to that of the diastereomers in the starting material (Scheme 6). Individual products **14a** and **14b** were isolated by preparative TLC and their structures were unambiguosly established by ^1H and ^{13}C NMR data.



SCHEME 6

Because the cycloadducts **14a** and **14b** differ only in a configuration of the $ArSCH_2$-substituents at C-8, one may assume that the IMPK cyclization of both diastereomers **12a** and **12b** proceeded with high diastereoselectivity. A rather different diastereoselectivity pattern was observed for the cyclization of the mixture **13a**,**b**, which furnished a mixture of three isomers **15a**,**b**,**c** in a ratio 4:2:1. In this case, the IMPK reaction of **13a** proceeded with a nearly complete diastereoselectivity to give the adduct **15a**, while the conversion of **13b** into the mixture **15b,c** exhibited a rather modest diastereoselectivity.

In summary, we elaborated a preparatively convenient protocol for the ready preparation of alkyne derivatives with the variable pattern of substitution secured by the use arylsulfenyl moiety first as an initiator and then as a group stabilizing a carbocationic intermediate. An opportunity to employ this approach for the concise synthesis of the substrates for IMPK reaction was also demonstrated.

REFERENCES

[1] K. M. Nicholas, *Acc. Chem. Res.*, **20,** 207 (1987).
[2] A. A. Schegolev, W. A. Smit, Y. B. Kalyan, M. Z. Krimer, and R. Caple, *Tetrahedron Lett.*, **23,** 4419 (1982).
[3] H. Mayr, O. Kuhn, C. Schlierf, and A. R. Ofial, *Tetrahedron*, **56,** 4219 (2000).
[4] S. L. Schreiber, T. Sammakia, and W. E. Crowe, *JACS*, **108,** 3128 (1986).
[5] T. J. J. Müller, *Eur. J. Org. Chem.*, 2021 (2001).
[6] N. E. Shore, *Org. React.*, **40,** 2 (1991); O. Geiss and H.-G. Schmaltz, *Angew. Chem., Int. Ed. Engl.*, **37,** 911 (1998).
[7] S. Shambayati, W. E. Crowe, and S. L. Schreiber, *Tetrahedron Lett.*, **37,** 5289 (1990).