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THE REACTION OF TERMINAL ALKYNES WITH THE REAGENT PREPARED FROM BENZENESELENENYL BROMIDE AND SILVER NITRITE. NOVEL EFFICIENT SYNTHESIS OF 1-ALKYNYL PHENYL SELENIDES

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1-Alkynyl phenyl selenides were synthesized in good yields by the reaction of 1-alkynes with a new reagent prepared from benzeneselenenyl bromide and silver nitrite.

1-Alkynyl selenides (1) are important intermediates for regiospecific and stereoselective synthesis of vinyl selenides.[1)] Two methods, both of which use 1-alkynes as the starting material, have thus far been available for the synthesis of these compounds (1).[1,2)] The earlier procedure utilizes the reaction of benzeneselenenyl bromide with lithium acetylide prepared with a strong base (e.g. butyllithium)[1)], which often presents cumbersome problems especially with cases involving base-sensitive substrates. The milder method, recently reported by us,[2)] involves Cu(I)-catalyzed reaction of 1-alkynes with phenyl selenocyanate. Although this allows the presence of the wider range of functional groups, serious drop of yield (37%) was observed with ethyl propiolate. Herein is reported an even milder method which was also successful in effecting the selenenylation of ethyl propiolate.

The new process, illustrated in Equation 1, involves the use of the nitro selenide reagent[3)] prepared from benzeneselenenyl bromide and silver nitrite. 1-Alkynes, including ethyl propiolate, react rapidly with this reagent under very mild conditions (r.t., 1–3 h) to provide 1-alkynyl phenyl selenides (1)[4)] in 67–85% yields (Table 1).

$$R\text{-}C{\equiv}C\text{-}H \xrightarrow[CH_3CN\ -\ CH_2Cl_2]{PhSeBr\ +\ AgNO_2} \underset{\underline{1}}{R\text{-}C{\equiv}C\text{-}SePh} \qquad (1)$$

In a typical reaction, a solution of silver nitrite (320 mg, 2.1 mmol) in dry acetonitrile (5 ml) was added to a stirred solution of benzeneselenenyl bromide (472 mg, 2.0 mmol) in dry dichloromethane (5 ml) at ambient temperature under nitrogen. At this time the dark brown solution of benzeneselenenyl bromide immediately turned pale yellow and the reaction mixture deposited precipitates of silver bromide. The contents were stirred for 5 min. Alkyne (2.0 mmol) was then added and the reaction mixture was stirred for further 1–3 h (TLC control).

It was then filtered through a filter paper to remove the precipitates. The concentrated filtrate was loaded onto a column of silica gel and eluted with a hexane-dichloromethane mixture. Concentration in vacuo afforded 1-alkynyl phenyl selenide (1) as colorless oil.

As shown in Table 1, this procedure is successful with a variety of alkynes to provide 1 in good yields which were not optimized. In particular ethyl propiolate gave a 74% yield of ethyl 3-phenylselenopropiolate (Entry 6).

Table 1. Synthesis of 1-Alkynyl Phenyl Selenides (1)

Entry	R	Reaction Time /h	Yield[a)] /%
1	$CH_3(CH_2)_3$-	1	78
2	$CH_3(CH_2)_5$-	1	85
3	$CH_3(CH_2)_7$-	3	77
4	$(CH_3)_2CH(CH_2)_2$-	3	85
5	$CH_3CH_2(CH_3)C(OH)$-	3	67
6	$CH_3CH_2O_2C$-	3	74
7	C_6H_5-	3	82

a) Isolated yield.

References

1) (a) S. Raucher, M.R. Hansen, and M.A. Colter, J. Org. Chem., 43, 4885 (1978); (b) N, Petragnani, R. Rodrigues, and J.V. Comasseto, J. Organometal. Chem., 114, 281 (1976). For recent ingenious synthetic applications of vinyl selenides, see; (c) M. Shimizu, R. Ando, and I. Kuwajima, J. Org. Chem., 46, 5248 (1981); (d) H. J. Reich, W.W. Willis, Jr., and P.D. Clark, J. Org. Chem., 46, 2775(1981).

2) S. Tomoda, Y. Takeuchi, and Y. Nomura, Chem. Lett., 1982, 253.

3) At this time we have not entirely been able to characterize the actual constituent of this reagent. However, it may formally be regarded as benzeneselenenyl nitrite and/or its tautomeric isomer. We therefore tentatively call this reagent "the nitro selenide reagent".

4) Structures of these compounds have been fully characterized previously.[2)]

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