

LETTERS TO THE EDITOR

Selenium- and Tellurium-containing Binucleophiles in Selective Synthesis of Allene and Methylacetylene from 2,3-Dichloro-1-propene

E. P. Levanova, V. S. Vakhrina, V. A. Grabel'nykh, N. V. Russavskaya,
A. I. Albanov, I. B. Rozentsveig, and N. A. Korchevin

*Favorskii Institute of Chemistry, Russian Academy of Sciences, Siberian Branch,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: venk@irioch.irk.ru*

Received August 5, 2013

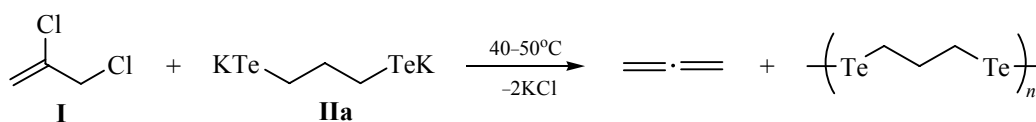
DOI: 10.1134/S1070363214010265

Allene and methylacetylene are important reagents in synthesis of unsaturated organic chemicals. Development of synthetic methods involving them often requires selective preparation of either allene or methylacetylene [1]. However, these isomers are readily interconverted or contaminated with the side products (usually, with propylene).

Recently, we have shown that pure allene is formed in the reaction of K_2Te_2 with 2,3-dichloro-1-propene (**I**) in the hydrazine hydrate – KOH medium [2]. In the case of Se analog (K_2Se_2), the reaction with compound **I** does not yield any gaseous products but rather gives bis(2-chloro-1-propene-3-yl)selenide [3].

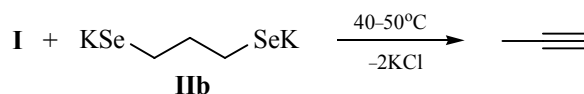
Extending the studies of chalcogen-containing nucleophiles reactions with **I**, we here report on the behavior of binucleophilic reagents, potassium 1,3-propanedithiuronate (**IIa**) and potassium 1,3-propanediselenate (**IIb**). Compounds **IIa** and **IIb** were prepared by reductive decomposition of the respective poly(trimethylenedichalcogenides) [4, 5] in the hydrazine hydrate–KOH medium. The so obtained salts **IIa** and **IIb** were introduced in the reaction with **I** without isolation.

1,3-Propanedithiuronate **IIa** reacted with dichloropropene similarly to K_2Te_2 , yielding allene (77% with respect to **I**) and regenerating the initial poly(trimethylenedithiuronate) (70% yield).



The so prepared allene contained only trace amounts (< 1.0%) of methylacetylene.

Under the same conditions, 1,3-propanediselenate **IIb** yielded methylacetylene containing traces of allene (< 0.5%). Se-containing products was a complex mixture of organoselenium compounds, their structures are under investigation and will be reported separately.



To conclude, change of the chalcogen nature allowed selective preparation of allene or methylacetylene via the reaction of potassium 1,3-propanedithiuronates with 2,3-dichloro-1-propene.

Allene. 4.82 g (0.016 mol) of poly(trimethylenedithiuronate) was added to the solution of 4.55 g (0.081 mol) of KOH in 20 mL of hydrazine hydrate upon stirring at 85°C. After polymer dissolution, the reaction flask was connected to two traps (–30 and –85°C), and 3.6 g (0.0324 mol) of 2,3-dichloro-1-propene was added dropwise at 40–50°C. 1.0 g of

allene was collected in the second trap. The product spectral parameters were identical to those reported in [2].

Methylacetylene was prepared similarly from 4.0 g (0.02 mol) of poly(trimethylenediselenide), solution of 5.61 g (0.10 mol) of KOH in 25 mL of hydrazine hydrate, and 4.44 g (0.04 mol) of 2,3-dichloro-1-propene. 1.0 g of methylacetylene was collected in the second trap. ^1H NMR spectrum (Bruker DPX 400, 400.13 MHz, solution in CDCl_3 , internal standard TMS), δ , ppm: 1.805 s ($\text{CH}\equiv$), 1.811 s (CH_3). ^{13}C NMR spectrum, δ , ppm: 3.16 (CH_3), 67.42 ($\equiv\text{CH}$), 80.01 ($-\text{C}\equiv$).

ACKNOWLEDGMENTS

This work was partially carried out using the facilities of the Collective Baikal Analytical Center (Russian Academy of Sciences, Siberian Branch).

REFERENCES

1. Taber, A.M., Mushina, E.A., Krentsel, B.A., *Allenovye uglevodorody: poluchenie, svoistva, primeneniye* (Allene Hydrocarbons: Preparation, Properties, and Application), Moscow: Nauka, 1987.
2. Levanova, E.P., Vshivtsev, V.Yu., Grabel'nykh, V.A., Sukhomazova, E.N., Russavskaya, N.V., Albanov, A.I., Tarasova, O.A., and Korchevin, N.A., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 10, p. 1980.
3. Levanova, E.P., Grabel'nykh, V.A., Russavskaya, N.V., Albanov, A.I., Elaev, A.V., Tarasova, O.A., and Korchevin, N.A., *Russ. J. Gen. Chem.*, 2011, vol. 81, no. 7, p. 1560.
4. Russavskaya, N.V., Levanova, E.P., Sukhomazova, E.N., Grabel'nykh, V.A., Elaev, A.V., Klyba, L.V., Zhanchipova, E.R., Albanov, A.I., Korotaeva, I.M., Toryashinova, D.S.D., and Korchevin, N.A., *Russ. J. Gen. Chem.*, 2006, vol. 76, no. 5, p. 726.
5. Russavskaya, N.V., Levanova, E.P., Sukhomazova, E.N., Grabel'nykh, V.A., Klyba, L.V., Zhanchipova, E.R., Albanov, A.I., and Korchevin, N.A., *Russ. J. Gen. Chem.*, 2006, vol. 76, no. 2, p. 229.