Tetrahedron Letters,Vol.24,No.21,pp 2203-2204,1983
Printed in Great Britain

0040-4039/83/212203-02$03.00/0

DIMETALATION OF ISOPROPENYLACETYLENE. APPLICATION IN THE SYNTHESIS OF 3-METHYLSELENOPHEN, 3-METHYLENE-2,3-DIHYDROSELENOPHEN AND THE TELLURIUM ANALOGUES

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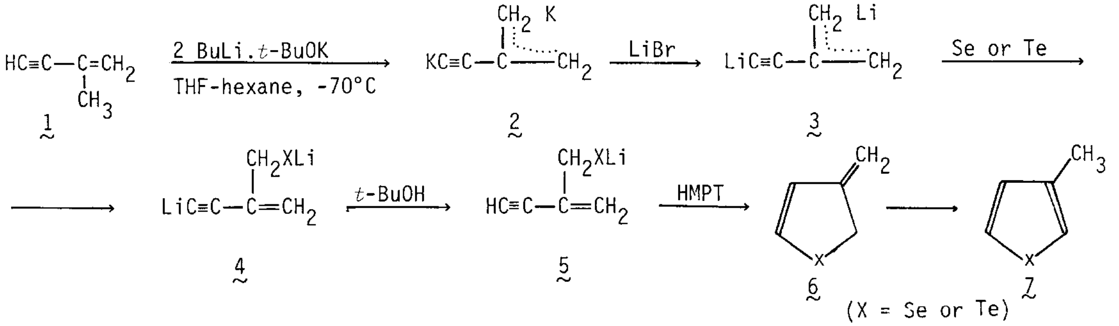
Abstract: Reaction of the dilithio derivative of isopropenylacetylene with one equivalent of selenium or tellurium, followed by addition of *t*-BuOH and HMPT gives 3-methylene-2,3-dihydroselenophen and 3-methylselenophen or 3-methylene-2,3-dihydrotellurophen in reasonable yields. The latter compound can be converted into 3-methyltellurophen by treatment with *t*-BuOK in HMPT.

As a result of our continued[1,2,3] study of unsaturated dimetalated compounds we wish to report the dimetalation of isopropenylacetylene 1 and the application in the synthesis of 3-methylselenophen, 3-methylene-2,3-dihydroselenophen and the corresponding tellurium compounds 6 and 7:



Addition at -70°C of a solution of 30 g *t*-BuOK in 50 ml of THF to a mixture of 1 (0.10 mol), butyllithium (0.27 mol in about 180 ml of hexane) and 110 ml of THF (obtained by adding 1 below -20° to the solution of BuLi in THF and hexane) gave an orange solution of 2. After stirring this solution for an additional 30 min at -70° the temperature was allowed to rise to -5°C. Anhydrous LiBr (0.25 mol in 60 ml of THF) was added, giving a light-yellow precipitate (3). Powdered red selenium or tellurium (0.11 at) was introduced in one portion at -45°C. The cooling bath was removed and the temperature was allowed to rise to 0°C. *Tert*-butylalcohol (for the amount see the table) was then added at -20°, followed by 50 ml of hexamethylphosphoric triamide (HMPT) at 0°C. The mixture was stirred for a period and at a temperature indicated in the table. Subsequent addition of ice water (500 ml), followed by the usual work-up (extraction with diethyl ether-pentane 1:1, washing with water, drying over $MgSO_4$ and careful distillative removal of the solvents at normal pressure) gave 3-methylselenophen and 3-methylene-2,3-dihydrotellurophen. 3-Methylene-2,3-dihydroselenophen was obtained in admixture with 3-methylselenophen. To obtain 3-methyltellurophen the dihydro compound (0.05 mol) was heated at 50°C during 1 h with a mixture of *t*-BuOK (0.01 mol), *t*-BuOH (0.006 mol), HMPT (10 ml) and THF (10 ml). After addition of water, extraction with ether, washing with water, drying over $MgSO_4$ the tellurophen was obtained in about 90% yield.

Compound*	b.p. °C/mmHg	n_D^{20}	Yield (%)	*t*-BuOH (mol)	reaction temp. (°C)	reaction time (min.)
6, X = Se**	58/11	1.6160	46	0.13	20	45
7, X = Se	28/15	1.5340	42	0.13	50	90
6, X = Te	87/11	> 1.71	51	0.26	55	45
7, X = Te	72/14	1.6267	90	-	-	-

* The ^{13}C and ^{1}H NMR data were in accordance with the structures. The purity (by G.L.C. and ^{1}H NMR) was at least 95%

** Ratio 6:7 about 9.

Although it has been known from previous investigations [4] that elemental selenium and tellurium smoothly react with alkali acetylides, the successful synthesis of 6 and 7 demonstrate that the elements discriminate satisfactorily between the two nucleophilic sites in 2 in favour of the more basic one. Reaction of 2 with dimethyldiselenide (one equivalent) followed by aqueous work-up gave $HC{\equiv}C{-}C(CH_2SeCH_3){=}CH_2$ as the sole isolable product,(b.p. 62°C/18 mmHg, n_D^{20} 1.5436) in 85% yield. In this case too there is complete regiospecificity with respect to the nucleophilic attack on selenium.

Our synthesis starting with the easily accessible isopropenylacetylene [5] represent a surprisingly facile access to the heterocycles 6 and 7 and it will probably be hard to find a more simple route.

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(Received in UK 17 March 1983)