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N EFFICIENT METHOD FOR THE CONVERSION OF 2-ALKYNYL THERS INTO ALLENIC ETHERS AND SOME α-SUBSTITUTED ERIVATIVES

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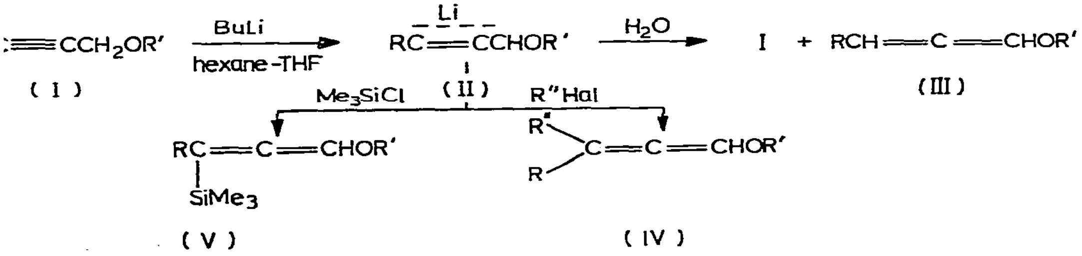
Reaction of 2-alkynyl ethers $RC{\equiv}CCH_2OR'$ with butyllithium and potas- um t-butoxide in THF, followed by addition of HMPT, gives the α-metal- ted allenic ethers $RCH{=}C{=}C(M)OR'$ (M is probably K). Subsequent addition water, alkyl halide, or trimethylchlorosilane affords the allenic ethers $CH{=}C{=}CHOR'$ and their derivatives $RCH{=}C{=}C(R'')OR'$ or $RCH{=}C{=}C(SiMe_3)$- R', respectively.

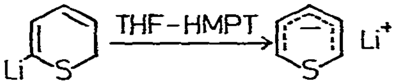
Conversion of 2-alkynyl ethers $RC{\equiv}CCH_2OR'$ (I) into allenic ethers $'CH{=}C{=}CHOR'$ (III) can be achieved by the catalytic action of bases like tassium t-butoxide or alkali amides if R is a group which has no or only e proton in the propargylic position (e.g. Ph, t-C_4H_9, cyclohexyl, $H_2C{=}C$- H_3) [1,2]. If R = primary alkyl, 1,4-elimination with formation of 3,1- ynes takes place [3]. To avoid this complication the 2-alkynyl ether can be hiated with butyllithium and the lithio derivative protonated (compare [4]). nfortunately protolysis is not regioselective and in most cases a mixture of lenic ether and starting compound, ratio varying from about 60/40 to about



70/30, depending to some extent upon the solvent in which the lithiation has been carried out [5], is obtained. We thus sought a more satisfactory way of convering I into III.

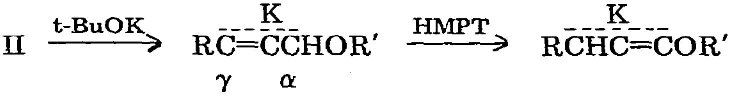
When to a solution of the lithiated 2-alkynyl ether II an equivalent amount of t-BuOK was added, subsequent hydrolysis gave a mixture of III and I, but with the more favourable ratio of about 85/15 for R = C_2H_5 or a higher alkyl group and R′ = alkyl or $CH(OCH_3)OC_2H_5$. Starting from $CH_3OCH_2C{\equiv}CCH_2N(C_2H_5)_2$ almost pure (⩾98%) $CH_3OCH{=}C{=}CHCH_2N(C_2H_5)_2$ was obtained; when the t-BuOK was omitted, protolysis afforded a 88/12 mixture of the allenic and acetylenic isomer in this special case.

We assume that upon addition of t-BuOK to the solution of II, Li is replaced by K (compare [6]), which may give rise to a change in the ratio of protonation at the alternative sites resulting from formation of III and I. Alkylation and trimethylsilylation of the presumed intermediate IIa led to the derivatives IV and V, respectively. A similar result was obtained by us and others [5] from the lithio derivative II. In order to effect a clean conversion of I into III we developed a procedure based on the finding [7] that addition of a sufficient quantity of hexamethylphosphoric triamide (HMPT) to a THF solution of 6-lithio-2*H*-thiopyran caused a complete transformation into the pentadienylic lithio derivative:



Other investigators [7] described similar transformations of lithio compounds under more polar, but seemingly aprotic conditions. In the light of those observation we envisaged the possibility of conversion of II into the potassio derivative VI, which could give pure allenic ethers III upon protolysis and the derivatives VII and VIII upon addition of alkyl halide and trimethylchlorosilane, respectively (compare similar results described in ref. [8] and [9]).

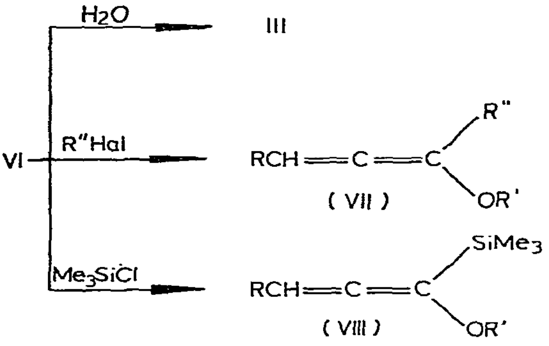
When some HMPT was added to the solution of IIa at about −80°C (at higher temperatures decomposition was observed), and then after about 20 min water, alkyl halide or trimethylchlorosilane was introduced, the pure allenic ether III and its derivatives VII and VIII, respectively were isolated in good yields. The products clearly arise from the potassio derivative VI, which means that we have succeeded in completely changing the γ-substitution in II and IIa into α-substitution via VI by increasing the polarity of the medium.



$$\mathrm{II}\xrightarrow{\text{t-BuOK}}\overset{\mathrm{K}}{\underset{\gamma}{\mathrm{RC}}{=}\underset{\alpha}{\mathrm{C}}}\mathrm{CHOR'}\xrightarrow{\text{HMPT}}\overset{\mathrm{K}}{\mathrm{RCHC{=}COR'}}$$

(IIa) (VI)

The mechanism by which the transformation of VI from IIa proceeds, is uncertain. One possibility is that the α-proton of one species IIa moves to the γ-position of another one as soon as the bond between the unsaturated part of IIa and potassium becomes more polar upon the addition of HMPT. Such a process might take place in a head-to-tail arrangement of two species IIa in an



aggregate structure. The functionalization of VI has limitations, addition of acetone, for example, did not give the desired α-carbinol. but largely unsubstituted allenic ether III. The same result was obtained when anhydrous lithium bromide was added to the solution of IIa before the addition of acetone. In the presence of the very polar HMPT the main reaction is probably metallation of acetone by IIa.

To prepare the compounds III, VII and VIII the 2-alkynyl ether I (0.05 mol) was dissolved in 30 ml of dry THF. Butyllithium (0.06 mol) in hexane (about 40 ml) was added with cooling between –50 and –60°C. The obtained solution was cooled to –85°C and a solution of t-BuOK (0.06 mol) in THF (30 ml) was added while maintaining the temperature between –80 and –90°C. Ten minutes after this addition 20 ml of dry HMPT (compare ref. 10, p. 140) were introduced with vigorous stirring and cooling around –85°C (in the case of $CH_3OCH_2C{\equiv}CCH_2N(C_2H_5)_2$, however, no HMPT was added and the solution was hydrolysed by addition of water). The brown solution was stirred for an additional 20 min at –85°C. Subsequently either water (150 ml), methyl iodide, propyl bromide (0.10 mol) or trimethylchlorosilane (0.08 mol) was added with vigorous stirring, the temperature being allowed to rise. In the case of Me_3SiCl, 5 ml of diethylamine were added as soon as the temperature of the reaction mixture had reached –30°C (this addition was carried out to ensure that no residual Me_3SiCl remained in the mixture, since this would give HCl during the aqueous work up, leading to reaction of the allenic ether with water). The products were isolated by addition of water, extraction with diethyl ether, washing of the extracts with water, drying over magnesium sulfate, and evaporation of the solvent in a water-pump vacuum.

The following compounds were prepared: $C_4H_9CH{=}C{=}CHOCH_3$, b.p. 61°C/20 mmHg, n_D^{23} 1.4468, yield 63%; $C_4H_9CH{=}C{=}C(CH_3)OCH_3$; b.p. 52°C/12 mmHg, n_D^{18} 1.4509, yield 68%; $C_4H_9CH{=}C{=}C(C_3H_7)OCH_3$; b.p. 75°C/15 mmHg, n_D^{20} 1.4535, yield 74%; $C_4H_9CH{=}C{=}C(SiMe_3)OCH_3$; b.p. 85°C/ 18 mmHg, n_D^{17} 1.4582, yield 72%; $C_2H_5CH{=}C{=}CHOCH(CH_3)OC_2H_5$, b.p. 65°C/12 mmHg, n_D^{18} 1.4463, yield 74%; $(C_2H_5)_2NCH_2CH{=}C{=}CHOCH_3$, b.p. 75°C/17 mmHg, n_D^{18} 1.4668, yield 75%.

The ^1H NMR spectra of these compounds were in agreement with their structures, and indicated a purity of at least 95%.

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