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A CONVENIENT METHOD FOR THE PREPARATION OF ALLENES FROM PROPARGYL ALCOHOLS USING 1-ETHYL-2-FLUORO-4,6-DIMETHYLPYRIDINIUM TETRAFLUOROBORATE

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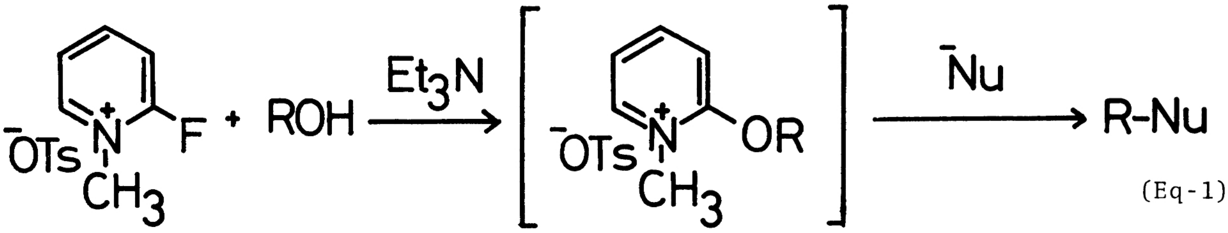
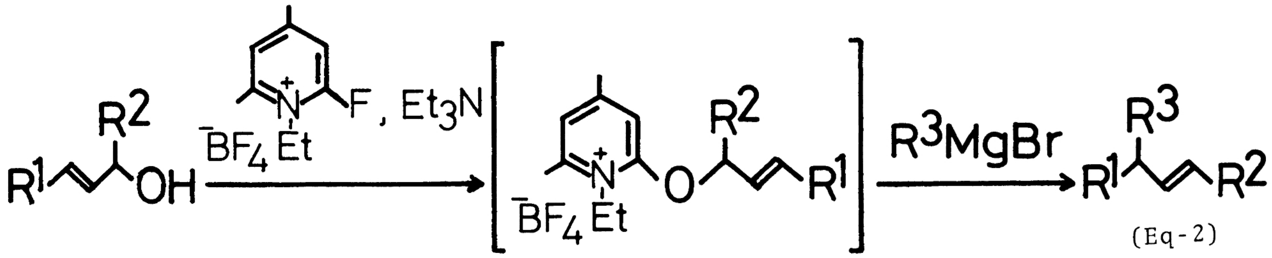
In the presence of a catalytic amount of copper(I) iodide, Grignard reagents reacted with 2-propargyloxypyridinium salts, formed in situ from propargyl alcohols and 1-ethyl-2-fluoro-4,6-dimethylpyridinium tetrafluoroborate, to produce various substituted allenes in good yields.

During the course of our investigation on the exploration of new reactions using the onium salts of azaaromatics,[1] it was found that various alcohols were directly converted to the corresponding substituted products by successive treatment with the onium salts and various nucleophiles, e.g., I^-, Cl^-, N_3^-, $Me_2NCS_2^-$, etc (Eq-1).[2]



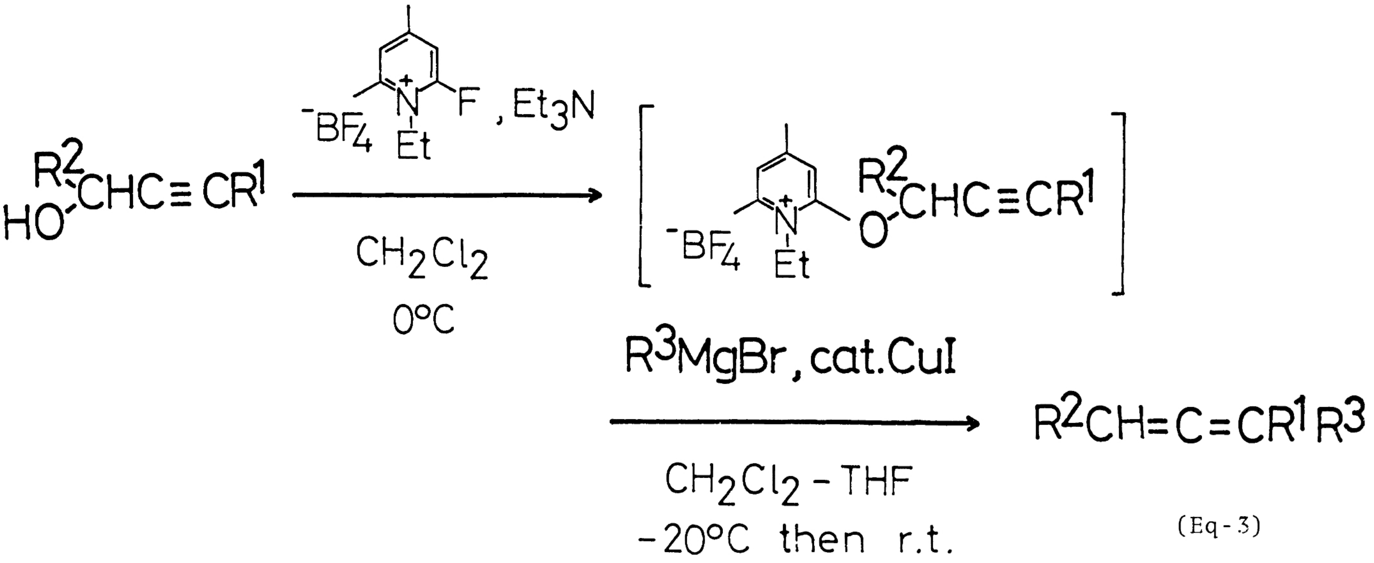
(Eq-1)

Furthermore, the previous paper[3] presented that 2-allyloxypyridinium salts, prepared in situ from allyl alcohols and 2-fluoropyridinium salts, reacted with Grignard reagents to give the corresponding olefins in good yields by a (formal) S_N2' displacement of pyridinoxy group to R^3(Eq-2).



(Eq-2)

The result suggests that when propargyl alcohols are employed instead of allyl alcohols in the above reaction, allenes would be produced by a similar displacement. In the present communication, we wish to report a useful method for the transformation of propargyl alcohols to pure allenes with the Grignard reagents in the presence of a catalytic amount of copper(I) iodide. As shown in the following equation(Eq-3), Grignard reagents in a cooled THF solution with a catalytic amount of copper(I) iodide smoothly reacted with 2-propargyloxypyridinium salts to afford allenes in high yields.

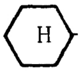
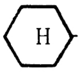
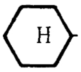
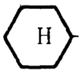
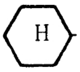


(Eq-3)

A typical procedure is described for the preparation of 1-cyclohexyl-5-phenyl-1,2-pentadiene: to a suspension of 1-ethyl-2-fluoro-4,6-dimethylpyridinium tetrafluoroborate[4] [1.2 mmol] in dichloromethane [1.5 ml] was added a mixture of 3-hydroxy-5-phenyl-1-pentyne [1.0 mmol] and triethylamine [1.2 mmol] in dichloromethane [1.5 ml] under an argon atmosphere and the mixture was stirred for 2 h at 0°C to give a clear yellow solution. The solution was added to a vigorously stirred mixture of cyclohexylmagnesium bromide [3.0 mmol] in THF [3 ml] and 5 mol % of copper(I) iodide at -20°C. After 20 min the temperature was allowed to rise to room temperature, followed by another period of stirring of 100 min. The reaction was quenched with saturated aq. ammonium chloride solution. The organic layer was extracted with dichloromethane and the extract was condensed under reduced pressure. The residue was chromatographed on silica gel, and 1-cyclohexyl-5-phenyl-1,2-pentadiene was obtained in almost quantitative yield.[5]

In a similar manner, various substituted allenes were prepared in good yields as summarized in the following Table.

Table. Yields of allenes

R^1	R^2	R^3	yield(%)
H	Ph-	$n\text{-}C_4H_9\text{-}$	90
H	Ph-		82
H	$PhCH_2\text{-}$	$n\text{-}C_4H_9\text{-}$	83
H	$PhCH_2\text{-}$		89
H	$PhCH_2CH_2\text{-}$	$n\text{-}C_4H_9\text{-}$	92
H	$PhCH_2CH_2\text{-}$		99
H	$PhCH_2CH_2\text{-}$	$t\text{-}C_4H_9\text{-}$	91
H	$n\text{-}C_8H_{17}\text{-}$	$n\text{-}C_4H_9\text{-}$	95
H	$n\text{-}C_8H_{17}\text{-}$		97
$n\text{-}C_4H_9\text{-}$	$PhCH_2CH_2\text{-}$	$n\text{-}C_4H_9\text{-}$	77
$n\text{-}C_4H_9\text{-}$	$PhCH_2CH_2\text{-}$		78
$n\text{-}C_4H_9\text{-}$	$PhCH_2CH_2\text{-}$	$t\text{-}C_4H_9\text{-}$	94

As shown in the Table, the reaction is successfully applied to terminal propargyl alcohols as well as nonterminal ones. One of the particular features of this reaction is that allenes prepared by the present method contain no acetylenes (S_N2 products), which usually contaminate allenes prepared by the other methods[6)] consisted of the reaction of the propargylic compounds $R^1R^2C(X)C{\equiv}CR^3$ such as chloride, bromide, acetate and tosylate with nucleophiles, for example, Grignard reagents or organocopper reagents via 1,3-substitution (S_N2') of the leaving group (X) by the nucleophile.

It should be noted that various allenes are prepared in good yields starting from propargyl alcohols by a simple procedure using the readily available pyridinium salt and Grignard reagents.

References and Notes

1) For example : K. Narasaka, T. Masui, and T. Mukaiyama, Chem. Lett., 1977, 763; T. Mukaiyama, N. Usui, E. Shimada, and K. Saigo, ibid., 1975, 1045; T. Mukaiyama, Y. Aikawa, and S. Kobayashi, ibid., 1976, 57; M. Shiono, Y. Echigo, and T. Mukaiyama, ibid., 1976, 1397.

2) S. Kobayashi, M. Tsutsui, and T.Mukaiyama, Chem. Lett., 1976, 373; T. Mukaiyama, S. Shoda, and Y. Watanabe, ibid., 1977, 383; K. Hojo, S. Kobayashi, K. Soai, S. Ikeda, and T. Mukaiyama, ibid., 1977, 635; K. Hojo, H. Yoshino, and T. Mukaiyama, ibid., 1977, 437.

3) T. Mukaiyama, M. Imaoka, and T.Izawa., Chem. Lett., 1977, 1257.

4) The onium salt was used after recrystallization from 1,2-dichloroethane. As for the present reaction, the simple pyridinium salt such as 1-ethyl-2-fluoropyridinium tetrafluoroborate is also available.

5) The analysis of the product by GLC showed a single peak.

6) P. Vermeer, J. Meijer, and L. Brandsma, Recl. Trav. Chim. Pays-Bas, 94, 113 (1975); J. L. Luche, E. Barreiro, J. M. Dollat, and P. Crabbe, Tetrahedron Lett., 1975, 4615; P. Crabbe, E. Barreiro, J. M. Dollat, and J. L. Luche, J. Chem. Soc., Chem. Commun., 1976, 183; D. J. Pasto, G. F. Hennion, R. H. Shults, A. Waterhouse, and S. K. Chou, J. Org. Chem., 41, 3496 (1976); ibid., 43 1385 (1978); D. J. Pasto, S. K. Chou, E. Fritzen, R. H. Shults, A. Waterhouse, and G. F. Hennion, ibid., 43, 1389 (1978).

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