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VINYL CATIONS, 17 [1]

ISOLATION OF AN INTERMEDIATE IN THE HOMOPROPARGYL REARRANGEMENT

Herbert Stutz and Michael Hanack*
Fachbereich 14, Organische Chemie, Universität des Saarlandes
66 Saarbrücken/Germany

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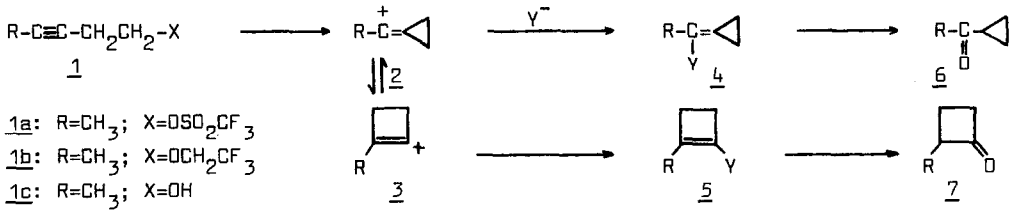
Homopropargyl compounds of type 1 (R=alkyl, X=OSO_2R') undergo solvolysis reactions in suitable solvents with participation of the triple bond to give cyclopropyl ketones 6 (R=alkyl) and cyclobutanones 7 (R=alkyl).[2] The formation of cyclic ketones 6 and 7 suggests the mechanism given in scheme 1 envisaging the formation of vinyl cations 2 and 3, which then react with the solvent (Y^-) to yield the ketones 6 and 7 via the corresponding enoles, enolesters or the enolethers 4 and 5 (Y=OH, OOC-R';OR') respectively.

Scheme 1



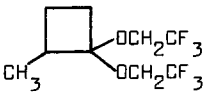
5a: R=CH_3; Y=OCH_2CF_3

Assuming the mechanism given in scheme 1 is correct,[2] it should be possible to isolate the intermediate cyclopropylidenemethyl-(4) and/or the cyclobutenyl-(5) products. Efforts directed towards this goal have remained unsuccessful. Our attempts to isolate the enol ester 4 or 5 (Y=OOCH; $OCOCF_3$) in the solvents allowing homopropargyl rearrangement (formic acid and trifluoroacetic acid) went unrewarded. Even in anhydrous solvents only the cyclopropylketones (6) and the cyclobutanones (7) were obtained.

We wish to report now that the solvolysis of pent-3-yn-1-yltrifluoromethanesulfonate 1a in 2,2,2-trifluoroethanol (TFE) has enabled us to isolate the cyclobutenyltrifluoroethylether 5a as the intermediate product.

In a typical experiment 0.65 g 1a (prepared from pent-3-yn-1-ol (1c) by treatment with trifluoromethanesulfonic acid anhydride in methylenechloride in the presence of anhydrous sodium carbonate) was dissolved in 2 ml of absol. TFE and with 0.66 g Na_2CO_3 as the buffer solvolyzed for 2 days at 30°C. (The half life of the triflate 1a in absol. TFE is 2 1/2 hours; calculated from $k_{30^0} = 7.51 \pm 0.17 \times 10^{-5} sec^{-1}$). As shown by gaschromatography the solvolysis products consisted of 86% 2-methylcyclobutene-1-yl-2',2',2'-trifluoroethylether 5a, 1% 2-Methylcyclobutanone 7, 2% of the ketal 8 and 4% pentynyltrifluoroethylether (1b).

5a was isolated by preparative gaschromatography. NMR spectrum (60MHz): δ=1.65 (m, 3H, CH_3-group); 1.94 (m, 2H, CH_2 in the cyclobutene ring); 2.49 (m, 2H, CH_2 in the cyclobutene ring); 4.10 (q, 2H, CH_2 in O-CH_2-CF_3, J=8.5Hz).



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For an additional structure proof, the ether 5a was treated for 5 min. with 1m-H_2SO_4 at room temperature, after which it was converted quantitatively into 2-methylcyclobutanone 7. The ketone 7, the ketal 8 as well as the trifluoroethylether 1b were also isolated by preparative gaschromatography and their spectra found to be identical with those of authentic samples. 2-Methylcyclobutanone-bistrifluoroethylketal 8: NMR spectrum (60MHz)δ= 1.13(d, 3H, CH_3-group); 2.10 (m, 5H, CH_2-groups of cyclobutane ring); 3.75 (q, 2H, CH_2-group in O-CH_2-CF_3); 3.83 (q, 2H, CH_2-group in O-CH_2-CF_3, J=8.5Hz).
The synthesis of 8 was carried out independently from 2-methylcyclobutanone and TFE in the presence of 2,2-dimethoxypropane [4] and a trace of p-toluenesulfonic acid in 45% yield.

The isolation of the cyclic enolether 5a is now an additional proof for the mechanism given in scheme 1 explaining the rearrangement of homopropargyl compounds to cyclic products by participation of the triple bond. The ketal 8 which is also formed in small amounts results from the addition of TFE to the double bond of the enolether 5a. This can be easily shown by the formation of 8 after treatment of the pure enolether 5a with TFE at room temperature. The formation of 5a through an addition-elimination mechanism can be ruled out in the case of TFE also, as this has already been done earlier using other solvents. Pentynole 1c does not add TFE to the triple bond under solvolysis conditions and the enolether 5a is not formed from the ketal 8 using the same conditions as in the solvolysis reactions.
For the homopropargyl rearrangement also, TFE due to its low nucleophilicity[5] is an especially suitable solvent for a cyclisation reaction. The cyclisation yields are highest if absolute TFE is used as a solvent. By adding water (80% TFE) the nucleophilicity of the solvent mixture is increased which leads to a clear decrease in the cyclisation yields ($\hat{=}k_\Delta$). Accordingly more of the non-rearranged substitution products are formed ($\hat{=}k_s$). The product composition from solvolysis of the triflate 1a in 80% TFE is as follows: 5a: 26%; 8: 1%; 7: 20%; 1b: 44%; 1c: 3%. The specific role of the buffers used on the cyclisation yields will be discussed elsewhere. It was found that in 97% TFE the buffer triethylamine can lead to a drastic decrease of the cyclisation yields.

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