Tetrahedron Letters,Vol.24,No.36,pp 3877-3878,1983
Printed in Great Britain

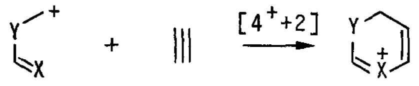
0040-4039/83 $3.00 + .00
© 1983 Pergamon Press Ltd.

POLAR CYCLOADDITION OF α-ACYL-α-CHLOROSULFIDES WITH ALKYNES. NOVEL ONE-STEP SYNTHESES OF FURANS AND 2-FURANONES

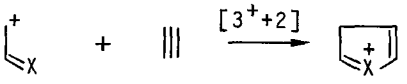
H. Ishibashi, S. Akai, H.-D. Choi, H. Nakagawa, and Y. Tamura
Faculty of Pharmaceutical Sciences, Osaka University
1-6 Yamada-oka, Suita, Osaka, 565 Japan

Summary: $[3^{+}+2]$ Polar cycloaddition of α-chloro-α-(methylthio)acetone (**1**) and methyl α-chloro-α-(methylthio)acetate (**2**) with alkynes in the presence of Lewis acid afford the furan derivative (**4**) and the 2-furanone derivative (**6** or **8**), respectively.

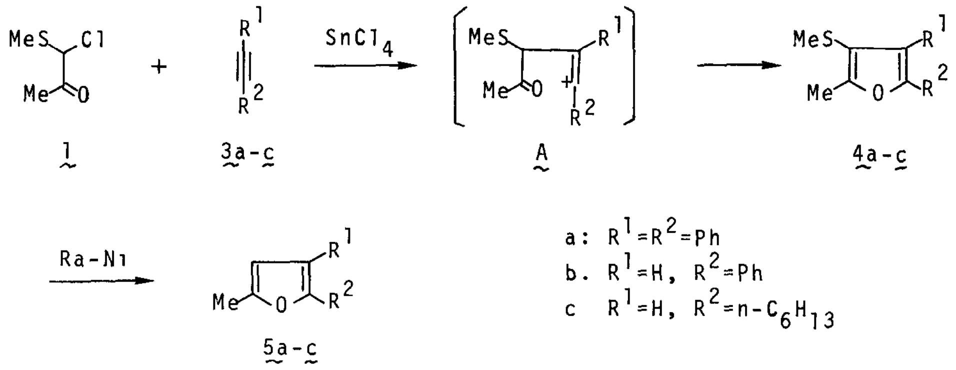
Much attention has recently been paid on an intramolecular trapping of the intermediary vinyl cations produced by electrophilic attack of carbocations to CC triple bonds. The $[4^{+}+2]$ polar cycloaddition shown in Scheme 1 is an example and provides a useful synthesis for various six-membered heterocyclic or carbocyclic compounds.[1] However, the corresponding $[3^{+}+2]$ polar cycloaddition (Scheme 2) has received scant attention.[2] In the present paper we wish to report a novel one-step syntheses of furan and 2-furanone derivatives by $[3^{+}+2]$ polar cycloaddition of the α-acyl-α-chlorosulfides 1 and 2 with alkynes.



Scheme 1



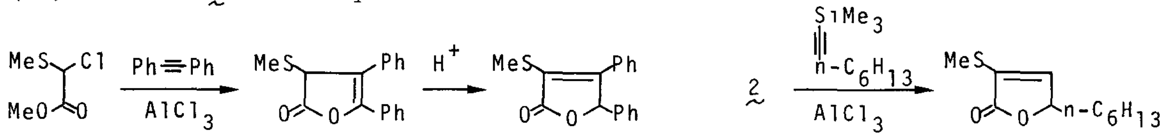
Scheme 2



Scheme 3

A solution of α-chloro-α-(methylthio)acetone (1, 1 mol eq), diphenylacetylene (3a, 1.2 mol eq), and $SnCl_4$ (2 mol eq) in CH_2Cl_2 was stirred at 0° for 3 hrs. After the usual work-up, chromatography on silica gel afforded 2-methyl-3-methylthio-4,5-diphenylfuran (4a) in 52% yield. Similar reactions with phenylacetylene (3b) and 1-octyne (3c) gave the furans 4b (35%) and 4c (40%), respectively. The structures of 4a-c were confirmed by their spectral data, and by direct comparison of authentic furans 5a-c with the compounds obtained by reductive desulfurization of 4a-c with W-7 Ra-Ni in CH_2Cl_2.[3] As formulated in Scheme 3, formation of the furan 4a-c is considered to proceed by electrophilic addition of the chloride 1 to the alkynes 3 and successive intramolecular nucleophilic attack of carbonyl oxygen to the resulted vinyl cations A.

The reaction of methyl α-chloro-α-(methylthio)acetate (2) with diphenylacetylene (3a) in the presence of $AlCl_3$ (2 eq) gave the 2(3H)-furanone 6[4] in 55% yield, which, on treatment with 10% HCl, was converted into the 2(5H)-furanone 7.[4] A similar reaction of 2 with 1-trimethylsilyl-1-octyne (3d) afforded the 2(5H)-furanone 8[4] in 26% yield.[5]



2 6 7 8

This conceptually novel [3+2] approach to furan and 2-furanone derivatives is thus simple, and its synthetic applicability seems highly promising.

REFERENCES AND NOTES

1) a) R. R. Schmidt, *Angew. Chem Int Ed Engl* , 12, 212 (1973); b) C. K. Bradsher, *Adv. Heterocyclic Chem* , 16, 289 (1974); c) Y. Tamura, K. Ishiyama, Y. Mizuki, H. Maeda, and H. Ishibashi, *Tetrahedron Lett* , 22, 3773 (1981), d) M. Karpf, *Tetrahedron Lett.*, 23, 4923 (1982).

2) a) G. J. Martin, Cl. Rabiller, and G. Mabon, *Tetrahedron Lett.*, 1970, 3131; b) P. Maroni and G. Melloni, *Tetrahedron Lett* , 1972, 2869.

3) 2-Hexyl-5-methylfuran (5c) can be further converted into dihydrojasmone *via* undecane-2,5-dione; see A. Takeda, S. Wada, M. Fujii, I. Nakasima, and S. Hirata, *Bull Chem Soc. Japan*, 44, 1342 (1971).

4) 6: mp 125-126°, IR ($CHCl_3$) 1760 cm^{-1}; NMR ($CDCl_3$) δ 1.97 (s, 3H, SMe), 6.51 (s, 1H, C_3-H), and 7.2-7.8 (m, 10H, arom). 7. IR 1755 cm^{-1}; NMR δ 2.61 (s, 3H, SMe), 6.22 (s, 1H, C_5-H), and 7.2-7.5 (m, 10H, arom). 8: IR 1760 cm^{-1}; NMR δ 0.7-2.1 [m, 13H, $(CH_2)_5Me$], 2.47 (s, 3H, SMe), 4.8-5.0 (m, 1H, C_5-H), and 5.64 (bs, 1H, C_4-H).

5) Mechanism of elimination of the trimethylsilyl group in this reaction is obscure at the moment. The reaction of 2 with 1-octyne (3c) did not give 8, but afforded a complex mixture of products.

(Received in Japan 31 May 1983)