Tetrahedron Letters,Vol.27,No.26,pp 3045-3048,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

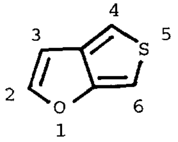
THE SYNTHESIS OF THIENO[3,4-*b*]FURAN USING A TANDEM INTRAMOLECULAR-REVERSE DIELS-ALDER REACTION APPROACH

JOHN MOURSOUNIDIS and DIETER WEGE*

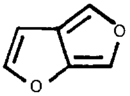
Department of Organic Chemistry, University of Western Australia, Nedlands,
Western Australia 6009.

Abstract. The title compound has been prepared by a route involving as the key steps the intramolecular Diels-Alder addition between a furan and a pendant acetylenic ester, and the subsequent retro-Diels-Alder fragmentation of the adduct, induced by 3,6-di(pyridin-2'-yl)-*s*-tetrazine.

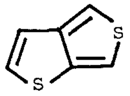
Thieno[3,4-*b*]furan (1), furo[3,4-*b*]furan (2) and thieno[3,4-*b*]thiophene (3) are heterocycles that may be classified as heteropentalenes in that they are isoelectronic with the formally aromatic pentalene dianion.[1]



(1)



(2)

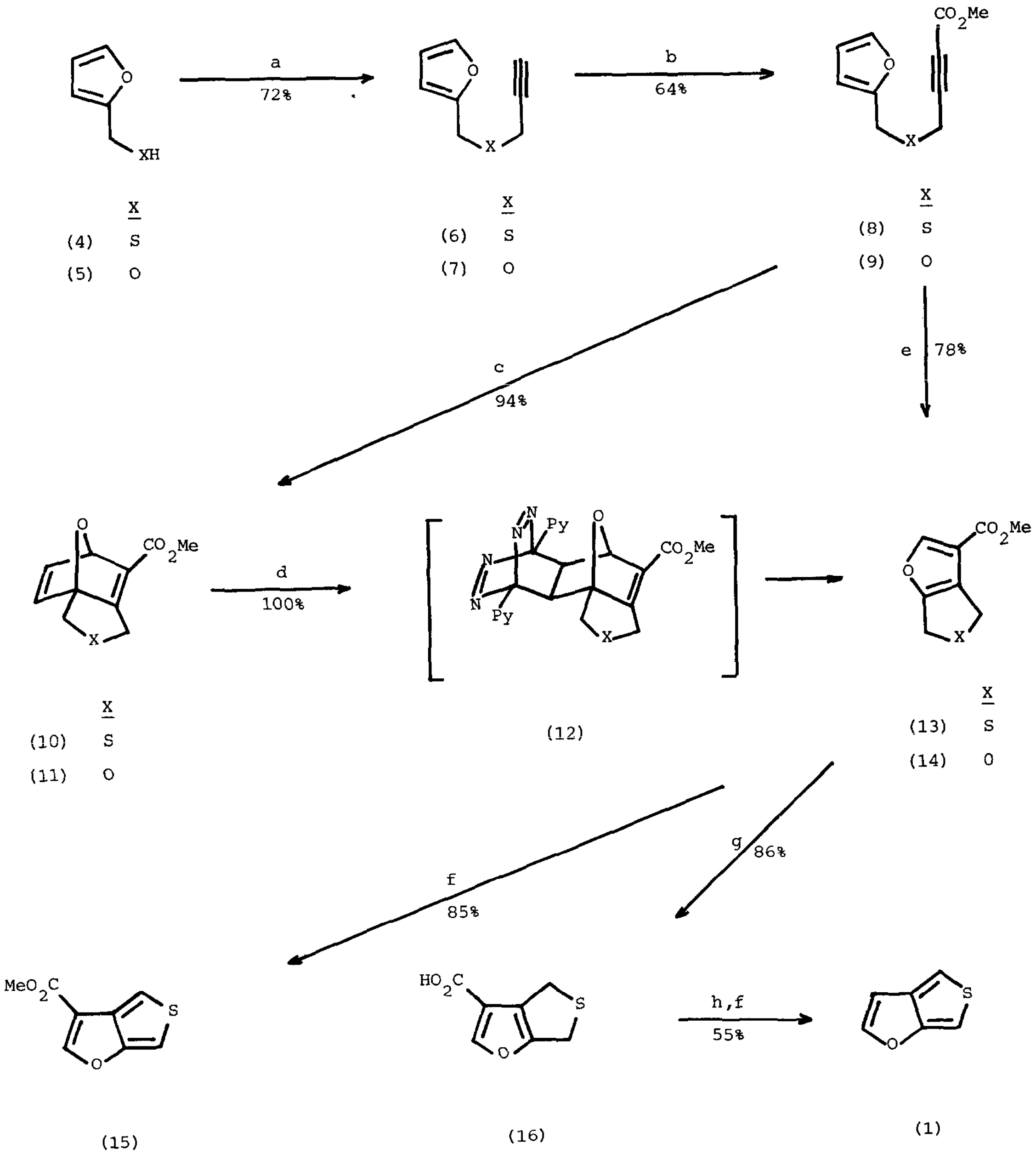


(3)

While (1)-(3) have all been included in a theoretical study of the aromatic stability of fused five-membered heterocycles,[2] only (3) is known,[3] although the preparation of the 4-phenyl-substituted derivative of (1) has been reported.[4] In this note we record the synthesis of (1) and an approach to (2) using a novel route involving sequential intramolecular and reverse Diels-Alder reactions.

The intramolecular Diels-Alder reactions of furans possessing pendant ethylenic dienophiles is a subject of intense current activity.[5] Arynes[6] and allenes[7] have also recently been successfully used as intramolecular traps for furans, but the use of acetylenic dienophiles has

SCHEME

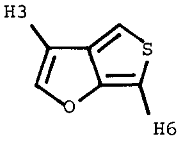


Reagents: a. NaH, THF, propargyl chloride, 25°, 2h; b. EtMgBr, THF, 0°, then $ClCO_2Me$; c. toluene, ↑↓, 14h; d. 3,6-di(pyridin-2'-yl)-s-tetrazine, $CHCl_3$, 60°, 40 min.; e. 3,6-di-(pyridin-2'-yl)-s-tetrazine, toluene, ↑↓, 15h; f. DDQ, CH_2Cl_2, 25°, 30 min.; g. HO^-, 60°, 2.5h, then H^+; h. Cu chromite, quinoline, 200°, 30 min.

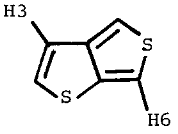
Yields refer to reactions where X = S.

not been studied in detail.[8] We find that the acetylenic ester (8), readily prepared from the thiol (4) as shown in the Scheme, in refluxing toluene affords the adduct (10), m.p. 56-9° (dec.). When (10) was warmed briefly in chloroform with the electron-deficient diene 3,6-di(pyridin-2'-yl)-*s*-tetrazine, the furan (13) was formed *via* the usual addition-cycloreversion sequence.[9] The intramolecular addition and cycloreversion steps can also be carried out by simply heating (8) with one equivalent of the dipyridyltetrazine in toluene. Activation of the acetylene by the methoxycarbonyl group is essential for intramolecular addition to occur, since the terminal acetylene (6) could not be induced to undergo reaction under these conditions.

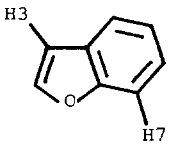
Brief treatment of the ester (13) with DDQ afforded methyl thieno[3,4-*b*]furan-3-carboxylate (15), m.p. 63-4°, ^{1}H n.m.r. ($CDCl_3$) δ 8.22, s, H2; 7.25, d, J 2.3 Hz, H4; 6.85, d, J 2.3 Hz, H6; 3.90, s, CO_2CH_3. The parent heterocycle (1) was prepared from (13) by a sequence involving ester hydrolysis, decarboxylation and dehydrogenation. Thieno[3,4-*b*]furan (1) was obtained as a colourless oil, ^{1}H n.m.r. (300 MHz, $CDCl_3$) δ 7.58, d, $J_{2,3}$ 2.4 Hz, H2; 6.92, d, $J_{4,6}$ 2.5 Hz, H4; 6.74, d of d, $J_{6,4}$ 2.4 Hz, $J_{6,3}$ 0.9 Hz, H6; 6.41, d of d, $J_{3,2}$ 2.5 Hz, $J_{3,6}$ 0.9 Hz, H3. The long range coupling observed between H3 and H6 is analogous to that found for thieno[3,4-*b*]thiophene (3)[3] and for benzofuran:[10]



$J_{3,6}$ = 0.9 Hz



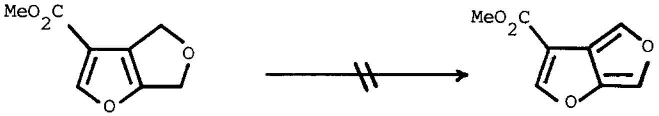
$J_{3,6}$ = 0.7 Hz



$J_{3,7}$ = 0.9 Hz

The electronic spectrum of (1) in ethanol shows λ_{max} 216 (log ε 3.65), 221 (sh) (log ε 3.62) and 259nm (log ε 3.74), and is essentially devoid of fine structure.

In an attempt to synthesise the furo[3,4-*b*]furan ring system of (2), we have carried out an analogous series of reactions starting with furfuryl alcohol (5) (Scheme). In this case the adduct (11) could not be isolated, but the tandem intramolecular reverse Diels-Alder sequence could be effected by refluxing (9) in toluene in the presence of dipyridyltetrazine. This afforded the ester (4), m.p. 129-30°, in 89% yield. However, all attempts to introduce the requisite additional unsaturation, either by dehydrogenation or bromination-dehydrobromination, have so far been unsuccessful. The preparation of (14) does however illustrate that the dipyridyltetrazine can be efficiently used to trap the adduct (11), despite the fact that (11) is presumably present only in low concentration in refluxing toluene. This tandem



(14) (17)

intramolecular-reverse-Diels-Alder reaction sequence should find application in other syntheses.

Acknowledgement. This work was supported by a grant from the Australian Research Grants Scheme.

References and Footnotes

1. M P Cava and M V Lakshmikantham, "Comprehensive Heterocyclic Chemistry", Vol. 4, p.1037 (C W Bird and G W H Cheeseman Eds, Pergamon Press: Oxford 1984).
2. M Milun and N Trinajstić, Croatia Chem. Acta, 1977, 49, 107.
3. H Wynberg and D J Zwanenburg, Tetrahedron Lett., 1967, 761. For the ^{1}H n.m.r. spectrum of (3) see H Wynberg and J Feijen, Rec. Trav. Chim., 1970, 89, 77.
4. A Shafiee and S Sattari, J. Heterocycl. Chem., 1982, 19, 227.
5. Reviews: G Brieger and J N Bennett, Chem. Rev., 1980, 80, 63; D F Taber, "Intramolecular Diels-Alder and Alder Ene Reactions" (Springer Verlag: Berlin 1984); A G Fallis, Canad. J. Chem., 1984, 62, 183; E Ciganek, Organic Reactions, 1984, 32, 1. For some other recent examples see M E Jung and L J Street, J. Am. Chem. Soc., 1984, 106, 8327; D D Sternbach, D M Rossana and K D Onan, Tetrahedron Lett., 1985, 26, 591; S J Burrell, A E Derome, M S Edenborough, L M Harwood, S A Leeming and N S Isaacs, Tetrahedron Lett., 1985, 26, 2229; L L Klein, J. Org. Chem., 1985, 50, 1770; L L Klein, J. Am. Chem. Soc., 1985, 107, 2573.
6. W M Best and D Wege, Tetrahedron Lett., 1981, 22, 4877; W M Best and D Wege, Aust. J. Chem., 1986 (in the press).
7. K Hayakawa, Y Yamaguchi and K Kanematsu, Tetrahedron Lett., 1985, 26, 2689.
8. Some experiments with acetylenic dienophiles have been reported: L A Van Royen, R Mijngheer, and P J De Clercq, Bull. Soc. Chim. Belg., 1984, 93, 1019. However, the adducts were either reluctant to form or decomposed readily.
9. W S Wilson and R N Warrener, J.C.S. Chem. Commun., 1972, 211.
10. P J Black and M L Heffernan, Aust. J. Chem., 1965, 18, 353.

(Received in UK 10 February 1986)