Tetrahedron Letters,Vol.27,No.24,pp 2757-2760,1986
Printed in Great Britain 0040-4039/86 $3.00 + .00
Pergamon Journals Ltd.

PHOTOOXYGENATION OF FURANS IN THE PRESENCE OF TRIMETHYLSILYL CYANIDE. OXIDATIVE CYANATION OF FURANS[1]

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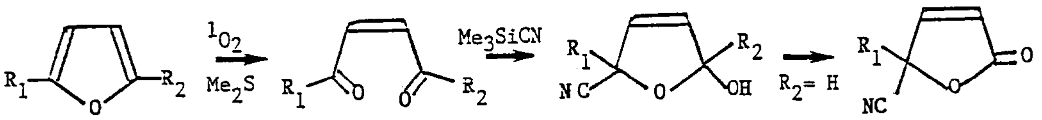
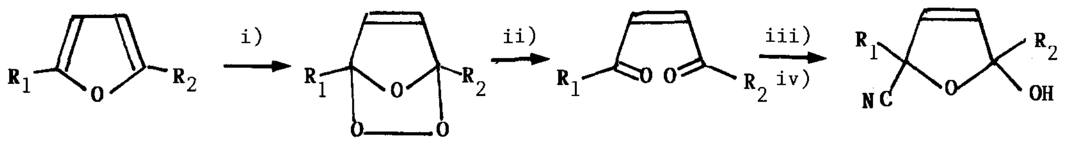
Summary: Low-temperature photooxygenation of furan derivatives followed by treatment with dimethyl sulfide and trimethylsilyl cyanide provides 2-cyano-5-hydroxy-2,5-dihydrofurans which are converted to 4-cyanobutenolides.

Photooxygenation of furans has been studied extensively from mechanistic and synthetic viewpoints.[2] Oxidative ring opening of furans leading to enediones is an important synthetic operation since furans can be used as masked 1,4-dicarbonyl units.[3,4,5] We recently demonstrated the use of a combination of singlet oxygen ($^1O_2$) and trimethylsilyl cyanide (TMSCN) for oxidative cyanation of certain electron-rich systems.[6] We now wish to report that low-temperature singlet oxygenation of furans followed by reduction with dimethyl sulfide (DMS) leads stereospecifically to cis-enediones which on subsequent treatment with TMSCN produce 2-cyano-5-hydroxy-2,5-dihydrofurans, the latter compounds being important precursors of 4-cyanobutenolides as illustrated below.



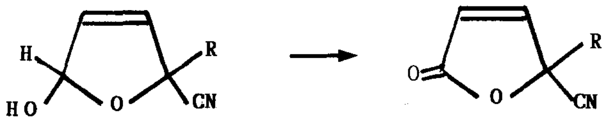
Tetraphenylporphine (TPP)-sensitized photooxygenation of 2- or 2,5-dialkylfurans **1** in CH_2Cl_2 at -70 °C produced instable furan endoperoxides **2** which were characterized by low--temperature NMR.[2c,7] Reduction of these endoperoxides with DMS in CH_2Cl_2 gave cis-enediones **3** stereospecifically. Unlike pyrrole endoperoxides,[6] addition of excess TMSCN to the endo-peroxides **2** in CH_2Cl_2 never produced the corresponding adducts. However, addition of DMS to a mixture containing TMSCN and endoperoxide followed by treatment with methanol produced 2-cyano-4-hydroxy-2,5-dihydrofuran **4**[8]. Alternatively, photooxygenation of furan **1** in the presence of TMSCN (2-3 equiv) in CH_2Cl_2 at -70 °C followed by addition of DMS gave 4. Control experiments indicated that cis-enediones 3 react very rapidly with TMSCN in CH_2Cl_2 in the presence of dimethyl sulfoxide (DMSO) to provide 4. Thus, it is clear that DMSO formed in situ by DMS reduction of endoperoxides acts as a catalyst for the formation of 4 from 3 and TMSCN. Usually, 4 were obtained in high yields when photooxygenated mixture was treated successively with DMS and TMSCN in CH_2Cl_2. The results are shown in the Table. It should be noted here that 4b,c,d,e were obtained regioselectively from 2-substituted furans.[9] In all these cases cis-enediones 3 were obtained in almost quantitative yields without TMSCN treatment. Note that reduction of furan endoperoxides with triphenylphosphine at 0 °C gave only trans-enediones.[2c] Conventional oxidation (PCC/CH_2Cl_2 or CrO_3/AcOH) of 4a,c,d gave 4-cyanobutenolides 5.[8]



1 2 3 4

a: $R_1 = R_2 = H$
b: $R_1 = CH_2OH$, $R_2 = H$
c: $R_1 = CH_2OAc$, $R_2 = H$
d: $R_1 = CH_2OBz$, $R_2 = H$
e: $R_1 = CHOHCH_3$, $R_2 = H$
f: $R_1 = R_2 = Me$
g: $R_1 = R_2 = CH_2OAc$
h: $R_1 = R_2 = CH_2OBz$

i) $^1O_2$/ CH_2Cl_2/ -70 °C ii) Me_2S iii) Me_3SiCN/cat. DMSO/CH_2Cl_2
iv) MeOH



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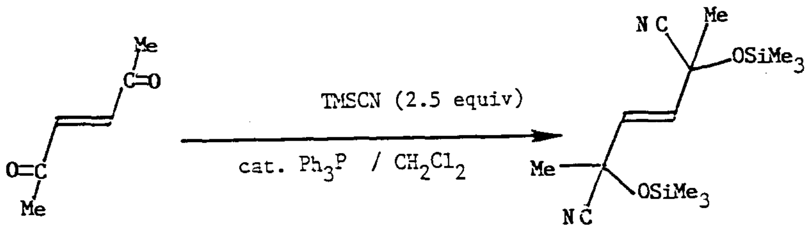
CrO_3/AcOH	55%	(R = H)
PCC/CH_2Cl_2	90%	(R = CH_2OAc)
	92%	(R = CH_2OBz)

In contrast, trans-enediones reacted only slowly with TMSCN in the presence of DMSO to give trimethylsilyl ethers of cyanohydrins. Such a transformation of enediones to trimethylsilyl ethers of cyanohydrins was achieved more conveniently by the catalysis of triphenylphosphine (TMSCN/cat. Ph_3P/ CH_2Cl_2/room temp) as exemplified below.[10]



6 95%

Table. Oxidative Cyanation of Furans[a]

Entry	Furan	Product[b]	Yield (%)[c]
1	1a	4a	91
2	1b	4b	65
3	1c	4c[d]	85
4	1d	4d[d]	92
5	1e	4e	82
6	1f	4f	87
7	1g	4g	90
8	1h	4h	92

[a]Experimental procedure is the same as described in the Text. [b]As a mixture of cis and trans adducts. The ratio is dependent on the reaction condition. Usually, the cis/tans ratio is ca. 2:3. For further transformation the mixture was used without purification. [c]Isolated yield. [d]As a mixture of 4 and its trimethylsilyl ether.

A typical experimental procedure is shown below. Furan (1a, 278 mg) and TPP (3 mg) were dissolved in anhydrous CH_2Cl_2 (15 mL). The solution was irradiated externally with bromine tungsten lamp at -70 °C under oxygen bubbling. After 2 h, DMS (1 mL) was added to the mixture under stirring. To this solution was added TMSCN (900 mg, 2.7 equiv) by use of syringe and the mixture was allowed to room temperature. Addition of methanol (1 mL) followed by silica gel column chromatography gave 4a as a 2:3 mixture of cis and trans adducts in 91%. The same photooxygenation at -70 °C followed by DMS reduction provided 3a quantitatively.

The present results demonstrate a novel use of singlet oxygen and trimethylsilyl cyanide for oxidative cyanation of substituted furans. Furthermore, inertness of TMSCN toward furan endoperoxides suggests that zwitterionic peroxide intermediates are not formed in the decomposition process of furan endoperoxides at least in CH_2Cl_2, in sharp contrast to the case of pyrrole endoperoxides.[6]

References and Notes

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8) These products gave consistent spectral data (IR, ^{1}H NMR and exact MS).

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(Received in Japan 25 February 1986)