Cycloaddition Reaction of Silver Ion Stabilized 6-Methoxycyclohepta-1-*cis*,-4-*trans*-diene

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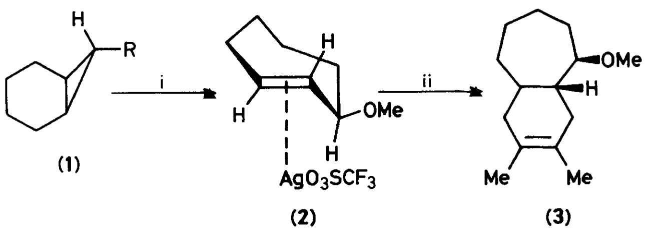
The title olefin, stabilized by complexation to silver trifluoromethanesulphonate, was used in a stereospecific [4 + 2]-cycloaddition.

trans-Cycloheptenes are short-lived intermediates in photochemical isomerizations of the corresponding *cis*-olefins.[1] In methanolic solution at room temperature, *trans*-cycloheptene has a lifetime of 45 s[2] and *trans*-cyclohept-1-en-3-one a lifetime of 0.03 s.[3] Their double bond deformations[4] induce a synthetically as well as mechanistically interesting, unique cycloaddition reactivity that is even further increased by additional ring contracting factors like endocyclic *cis*-double bonds or oxygen atoms.[5,6] Even *trans*-cyclo-octene, that is orders of magnitude less reactive[7] than *trans*-cycloheptene, has been used to achieve cycloaddition reactions with 1,3-dipolar compounds that would not react with other olefins.[8,9]

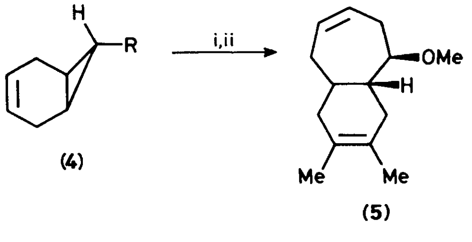
Unfortunately, the photochemical generation of *trans*-cycloheptenes is not suitable for conducting cycloaddition reactions because of interference from numerous side reactions (*i.e.* dimerizations, solvent additions, fast *trans* → *cis* isomerization, excitation of the cycloaddition partner, or cycloaddition of photoexcited *cis*-olefin).[1]

Recently we prepared and utilized the silver trifluoromethanesulphonate (triflate) complex of stereospecifically substituted *trans*-cycloheptenes for some cycloaddition reactions (Scheme 1).[10] In the sequence (**1**)—(**3**), the silver ion performs several functions: (a) it catalyses the deamination of norcarane nitrosourea (**1**) and renders a base unnecessary, (b)



R = -N(NO)-CONH$_2$

Scheme 1. i, AgO$_3$SCF$_3$, MeOH, 0 °C; ii, CH$_2$=C(Me)-C(Me)=CH$_2$, MeOH, 25 °C.



R = -N(NO)-CONH$_2$

Scheme 2. i, AgO$_3$SCF$_3$, MeOH; ii, CH$_2$=C(Me)-C(Me)=CH$_2$, MeOH.

it stabilizes the *trans*-cycloheptene by complexation and allows for the isolation of (**2**),[10] (c) it probably catalyses the [4 + 2]-cycloaddition of the *trans*-cycloheptene by pre-coordination of the diene.[10,11] Conveniently, the more strained (5*RS*,6*RS*)-6-methoxycyclohepta-1(*Z*),4(*E*)-diene can be used, avoiding the losses associated with the isolation of the silver complex.

Using a similar procedure to that in Scheme 1, compound (**4**)[12] was stirred with 2 equiv. of silver triflate (MeOH, 0 °C, dark, 24 h). The reaction mixture was filtered and the filtrate concentrated *in vacuo*. 1.2 Equiv. of 2,3-dimethylbuta-1,3-diene was added and the saturated methanolic solution stirred at 25 °C (dark, 24 h). The solvent and excess of diene were then removed *in vacuo*; product (**5**) was obtained in 65% yield (vacuum transferred at 25 °C) (Scheme 2).†

We are investigating the use of this method for the synthesis of natural products containing *trans*-annellated seven membered rings.

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† Spectroscopic data for (**5**): ^{13}C n.m.r. ($CDCl_3$): δ 132.91, 126.34, 124.78, 124.74, 83.51, 56.20, 48.75, 41.46, 38.21, 37.52, 34.46, 29.80, 18.53, 18.44; ^{1}H n.m.r. (CCl_4, 90 MHz): δ 5.94—5.40 (m, 2H), 3.20 (s, 3H, OCH_3), 2.83—2.60 (m, 1H, 2-H), 2.40—1.30 (m, 10H), 1.54 (s br., 6H, 2 × CH_3); i.r. (CCl_4): 3030, 1658(w), 1097(s), 717 cm^{-1}; *m/z* 206.16715 (M^+, calc. 206.16707). The stereochemistry of the methoxy group in (**5**) corresponds to a preservation of the *trans,trans* relationship of the cyclopropyl protons in (**4**). See also: G. H. Whitham and M. Wright, *J. Chem. Soc. C,* 1971, 883; C. B. Reese and A. Shaw, *J. Chem. Soc., Perkin Trans. 1,* 1975, 2422; W. Kirmse and H. Jendralla, *Chem. Ber.*, 1978, **111**, 1857.

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