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Intramolecular Cyclopropanation of 7-Diazotethered-1,3,5-Cycloheptatriene: Preparation and Reactions of Tricyclo[5.3.0.$0^{2,10}$]deca-3,5-dien-9-one

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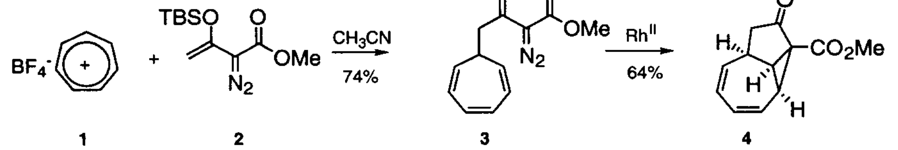
Abstract: The rhodium(II)-catalyzed diazo decomposition of 7-diazocarbonyltethered-1,3,5-cycloheptatriene **3** generated tricyclic ketoester **4** in 64% yield. Reaction of ketoester **4** with nucleophiles leads to cyclopropane cleavage (Nu = PhSNa) to give **5** or rearrangement (Nu = RNH_2) to give **7** or **8**. © 1997 Elsevier Science Ltd.

We recently initiated a research program[1] which merges the use of transition metal π-complexes[2] with the diazodecomposition of α-diazocarbonyl compounds,[3] two well-known approaches to modern organic synthesis. Although the diazodecomposition of α-diazocarbonyl compounds in the presence of olefins typically generates cyclopropanes, complexation of the π-system to a transition metal renders these olefins unreactive.[1] As part of our overall study we have also begun to examine diazodecomposition reactions of α-diazocarbonyl compounds tethered to non-complexed unsaturated cyclic systems. Although diazodecomposition reactions of α-diazocarbonyl compounds tethered to olefins, dienes, and even trienes have been reported,[3,4] the literature contains less information about decompositon reactions of α-diazocarbonyl compounds tethered to unsaturated cyclic systems.[5-7] It appeared that manipulation of the highly strained tricyclic cyclopropanes derived from such reactions might present opportunities for elaboration to important intermediates for organic synthesis. For example, nucleophilic attack on electron deficient cyclopropanes is well-known, and has been utilized in the synthesis of several natural products.[7] We chose initially to investigate systems derived from 7-substituted-1,3,5-cycloheptatrienes, and report herein our preliminary results.[8]

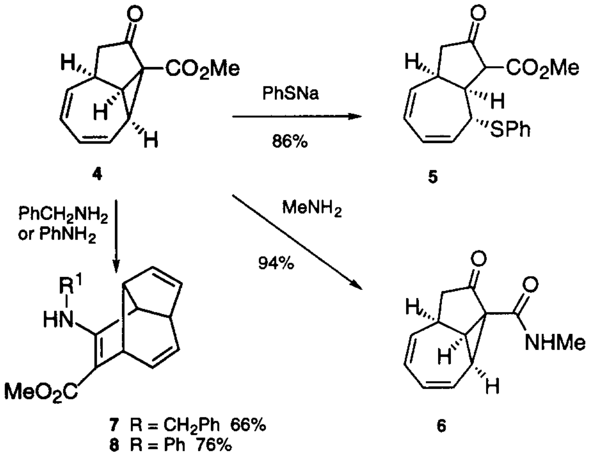
The most logical route to the desired α-diazocarbonyl-tethered precursor **3** appeared to involve the reaction of tropylium cation **1** with an appropriate nucleophile. Reaction of tropylium cation **1** with enol silyl ether **2**[9] provided 7-diazotethered-1,3,5-cycloheptatriene **3**[10] in 74% yield in one step (Eq. 1). Diazodecomposition of cycloheptatriene **3** using catalytic amounts of rhodium(II) hexanoate in a 1:1 mixture of dichloromethane and benzene provided the desired tricyclic ketone **4** in 64% yield. An x-ray crystal structure of ketoester **4** confirmed the all *syn* ring fusion.[11]



1 **2** **3** **4** (1)

With a suitable route to tricyclic compound **4** in hand, investigation of the reactivity of this material was undertaken. As expected, reaction of **4** with sodium phenylthiolate in tetrahydrofuran provided *cis*-fused bicyclo[5.3.0]deca-4,6-dien-2-one **5** in 86% yield (Scheme 1). Nucleophilic attack appears to take place specifically at the less hindered face of the cyclopropane.[7] The resulting anti relationship between the phenylthio substituent and the cyclopentyl moiety was confirmed by ^{1}H NMR nOe data.[12] Although molecular mechanics calculations indicate that the more stable compound contains the ester moiety in the α configuration, ^{1}H NMR coupling and nOe data from compound **5** proved inconclusive. Reaction of ketoester **4** with several organocuprates and methoxide also appeared to provide products resulting from ring opening of the cyclopropane, but these products were quite unstable, and attempts to isolate material suitable for proper characterization were unsuccessful.

Scheme 1

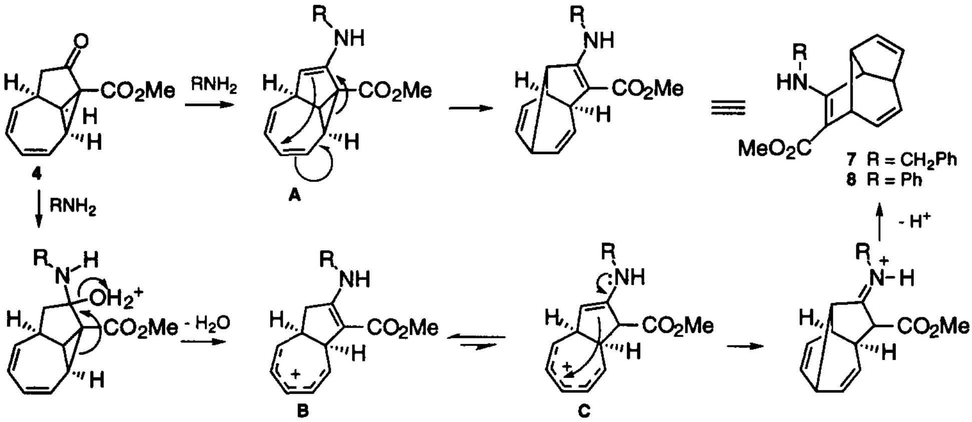


Reaction of ketoester **4** with amines produced completely different results. Reaction of tricyclic ketoester **4** with excess aqueous methylamine in THF generated amide **6** in 94% yield. No evidence of attack at the cyclopropane was noted, even at higher reaction temperatures. Reaction of ketoester **4** with benzylamine or aniline provided products which did not match either the phenylthiolate adduct **5** or the methylamine product **6**. Although the ^{1}H NMR spectra of each of these materials clearly contained four vinyl hydrogens, decoupling data indicated that the two olefins were not conjugated (as required for products such as **5** and **6**). Infrared spectra of these materials contained no peaks in the region expected for ketones or esters (1710-1745 cm^{-1}), but did contain peaks at 1675 cm^{-1}, corresponding to a vinylogous carbamate. Careful analysis of the ^{1}H, ^{13}C NMR, and IR data pointed to the proposed tricyclo[5.3.0.0^{4,8}]deca-2,5,9-trienes **7**[10] and **8**. Although a mechanistic study of this reaction has not been carried out, tricyclic compounds **7** and **8** may arise by formation of enamine **A** (Scheme 2) followed by a divinylcyclopropane rearrangement.[13] Another possible mechanism for this transformation involves attack of the amine at the ketone followed by cyclopropane cleavage with concomitant loss of water to form the cationic species **B** (Scheme 2). Intramolecular attack of the enamine **C** at the central carbon of the dienyl cation, followed by tautomerization provides tetracyclic materials **7** or **8**.[14] A thorough examination of these reactions currently is underway, as is the use of this sequence to provide facile access to functionalized bicyclo[5.3.0]deca-4,6-dienes and tricyclo[5.3.0.0^{4,8}]deca-2,5,9-trienes.

Selected Experimental

Methyl 4-[7-(1,3,5-cycloheptatrienyl)]-2-diazo-3-oxobutanoate 3. A solution of 0.870 g (5.00 mmol) of tropylium tetrafluoroborate (**1**) in 11 mL of acetonitrile was cooled to 0 °C under argon. To this solution was added dropwise a solution of 1.71 g (7.50 mmol, 1.5 eq) of silyl enol ether **2**[9] in 2 mL of

Scheme 2



acetonitrile. The mixture was stirred at 0 °C for 15 min, and then at rt for 30 min. The solvent was evaporated under reduced pressure and the residue chromatographed (silica, 10:1 hexane/ethyl acetate) to give 0.861 g (74%) of **3** as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 6.64 (dd, J = 3.5, 2.8, 2 H), 6.18 (dm, J = 10.1, 2 H), 5.22 (dd, J = 5.8, 8.9 Hz, 2 H), 3.83 (s, 3 H), 3.23 (d, J = 7.4, 2 H), 2.30 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 191.2, 161.7, 131.0, 125.1, 125.0, 52.2, 43.1, 34.9. IR (neat) 2144, 1729, 1704, 1652 cm^{-1}. Anal Calcd for $C_{12}H_{12}N_2O_3$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.33; H, 5.44; N, 11.83.

8-(Benzylamino)-9-(carbomethoxy)-tricyclo$[5.3.0.0^{4,8}]$deca-2,5,9-triene 7. A mixture of 0.106 g (0.519 mmol) of ketoester **4** and 0.177 g (1.65 mmol, 3.2 eq) benzylamine in 4 mL of benzene was heated under reflux for 2 h. The solvent was then removed under reduced pressure and the residue chromatographed (alumina, 5:1 hexane/ethyl acetate) to give 0.101 g (66%) of **7** as a light yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.60 (bs, 1 H), 7.15-7.35 (m, 5 H), 6.57 (dd, *J* = 5.7, 2.8 Hz, 1 H), 6.01 (ddt, *J* = 9.2, 5.3, 1.0 Hz, 1 H), 5.77 (ddt, *J* = 9.2, 5.5, 1.0 Hz, 1 H), 5.57 (dd, *J* = 5.7, 2.9 Hz, 1 H), 4.37 (d, *J* = 6.5 Hz, 2 H), 3.70 (s, 3 H), 3.24 (m, 2 H), 2.84 (dd, *J* = 5.2, 4.2 Hz, 1 H), 2.25 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 168.0, 163.0, 145.4, 139.1, 134.5, 128.9, 128.7, 128.5, 127.2, 126.5, 107.8, 57.9, 56.1, 50.1, 48.3, 41.1, 38.4. IR (neat) 3329, 3030, 2947, 1654, 1599 cm^{-1}. HRMS *m/z* calcd for $C_{19}H_{19}NO_2$ $[M]^+$ 293.1416, obsd 293.1418.

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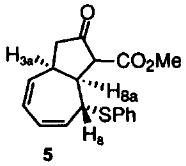
8. All new compounds were characterized by spectroscopic data, including ^{1}H NMR, ^{13}C NMR, and infrared spectra, and elemental analysis or high resolution mass spectra.
9. Davies, H.M.L.; Houser, J.H.; Thornley, C. *J. Org. Chem.* **1995**, *60*, 7529.
10. Please see the Selected Experimental section for the experimental procedure and spectroscopic data for this compound.
11. The author has deposited atomic coordinates for **4** with the Cambridge Crystallographic Data Center. The coordinates can be obtained on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2, 1EZ, UK.
12. In addition to literature precedent for attack by sodium phenylthiolate at the less hindered face of the cyclopropane,[7] ^{1}H NMR data supported the proposed structure of **5**. A 500 MHz NOESY experiment showed no enhancement between H_8 and H_{3a}, but did show enhancement between H_{8a} and the ortho phenylthio hydrogens.



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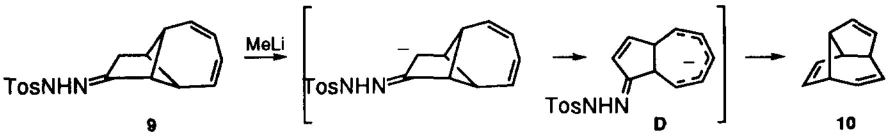
13. Divinylcyclopropane rearrangements of related systems have been reported. See for example (a) Vedejs, E.; Wilber, W.R.; Twigg, R. *J. Org. Chem.* **1977**, *42*, 401. (b) Vedejs, E.; Shepherd, R.A.; Steiner, P. *J. Am. Chem. Soc.* **1970**, *92*, 2158.
14. A related rearrangement, which occurs during the Shapiro reaction of the tosylhydrazone of tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one **9** (Eq. 2), generates tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene (**10**). The authors report that this reaction proceeds via bicyclo[5.3.0]decatrienyl intermediate **D**. See Gleiter, R.; Zimmermann, H.; Sander, W.; Hauck, H. *J. Org. Chem.* **1987**, *52*, 2644.



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