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REACTIONS OF TRIFLUOROMETHYLCYCLOPENTADIENE, 2-PROPYN-1-OL, AND BASE

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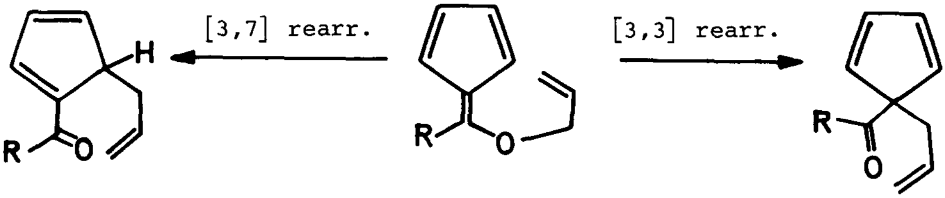
Trifluoromethylcyclopentadiene, 2-propyn-1-ol, and base can give either propynyl 5-allenyl cyclopentadienecarboxylate, 1 , or tri(2-propynyl) cyclopentadieneorthocarboxylate, 2. The latter undergoes an intramolecular Diels-Alder reaction to the norbornadiene derivative 3a.

Claisen rearrangements of allyl vinyl ethers and allyl aryl ethers are important tools for the synthesis of natural products and other complex compounds.[1] The reaction is concerted and classified as a [3,3] sigmatropic reaction.[2] The Claisen rearrangement of aryl allyl ethers usually requires elevated temperatures and longer reaction times due to the loss of resonance energy in the transition state. The rearrangement of an allyl fulvenyl ether should require less energy. Two competing reactions are possible, a [3,3] and a [3,7] sigmatropic reaction.

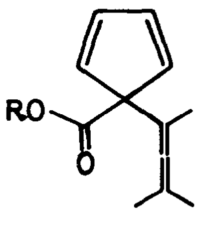


Trifluoromethylcyclopentadiene is a useful starting material for the synthesis of 6,6-disubstituted fulvenes. It can readily be prepared from nickelocene and trifluoroiodomethane.[3] In the presence of base it reacts with a variety of nucleophiles to give 6,6-disubstituted fulvenes, presumebly via the very reactive intermediate 6,6-difluorofulvene. Bifunctional nucleophiles, base, and trifluoromethylcyclopentadiene give fulvenes with an extra ring; 1,2-ethanediol gives the cyclic ketal of carbonylcyclopentadiene.[3]

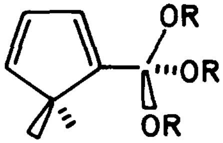
We have recently prepared 6-allyloxyfulvenes by this method and found that they rearrange rapidly and selectively by a normal Claisen reaction to give 5-allylcyclopentadienes.[4] In order to further examine the possibility of a [3,7] sigmatropic reaction as compared to the common [3,3] rearrangement we have reacted trifluoromethylcyclopentadiene, 2-propyn-1-ol, and base. The geometry of the propynyl group should enhance the [3,7] rearrangement, which occurs *via* a seven-membered ring in the transition state, over the normal [3,3] rearrangement, which occurs *via* a six-membered transition state.

Trifluoromethylcyclopentadiene in ether was added to three equivalents of sodium in 2-propyn-1-ol. The product (after washing with water and chromatography on silica gel with dichloromethane as eluant) was identified as propyny 5-allenylcyclopentadienecarboxylate, 1 (70 %), *i.e.* the product from a normal Claisen rearrangement [NMR ($CDCl_3$, 270 MHz): δ 6.44 (2 H) and 6.39 (2 H) AA´BB´-pattern, cyclopentadienyl protons, 5.40 (1 H, t, *J* 6.5 Hz) and 4.83 (2 H, d, *J* 6.5 Hz) allenyl protons, 4.65 (2 H, d, *J* 2.5 Hz) and 2.48 (1 H, t, *J* 2.5 Hz) propynyl ester protons. MS (70 eV): *m/e* 186 (8 %, M^+), 147 (84, $M^+ - C_3H_3$), 120 (25), 119 (70), 105 (34), 103 (52), 102 (36), 91 (61), 78 (36), and 77 (100). Abs. mass 186.065; calc. for $C_{12}H_{10}O_2$ 186.068]. Small amounts of vinylfulvene are also formed, presumebly *via* cleavage of the ester followed by decarboxylation and, finally, rearrangement of the allenylcyclopentadiene to the more stable vinylfulvene. No product from a [3,7] sigmatropic rearrangement of a propynyloxyfulvene was observed.

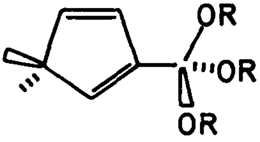
When trifluoromethylcyclopentadien was treated with more than four equivalents of base in 2-propyn-1-ol, no product from a Claisen rearrangement was observed. The product (isolated by washing the ether solution with water and rapid chromatography on deactivated silica gel with dichloromethane) was a mixture of tri(2-propynyl) 1- and 2-cyclopentadieneorthocarboxylates, 2a and 2b, in almost quantitative yield [NMR ($CDCl_3$, 270 MHz): δ 6.9-6.5 (3 H, m) olefinic protons, 4.17 (6 H, d, *J* 2.5 Hz) and 2.36 (3 H, t, *J* 2.5 Hz) propynyl protons, 3.10 (2 H, m) methylene protons].



1



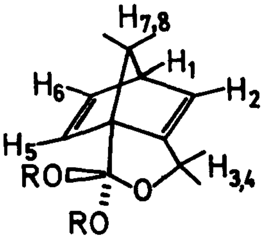
2a



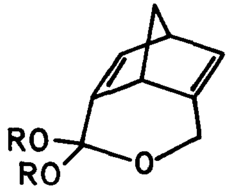
2b

The facile formation of an ortho ester by a nucleophilic attack of an alkoxide ion of a 6,6-dialkoxyfulvene clearly shows the high reactivity of the exocyclic double bond caused by the resonance stabilisation of the cyclopentadienyl anion. Ortho esters are sometimes formed by other reactions on treatment of trifluoromethylarenes with alkoxide.[5] The stability of the ortho esters 2a and 2b is in sharp contrast to that of cyclopentadiencarboxylic esters, which dimerise instantaneously. Clearly, the cyclopentadiene ring is much more activated for a Diels-Alder dimerisation by a conjugated carbonyl group than by a strongly electron-withdrawing group.^{6}

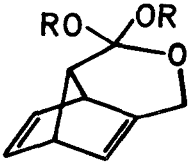
On standing in solution ($CDCl_3$, 10-15 %, 7 days, room temp.), the isomeric mixture of the ortho esters gives a single new product quantitatively. The product has the same molecular weight as the ortho esters but the NMR spectrum shows the disappearance of one of the propynyl groups and the cyclopentadiene ring and also the appearance of a complex spin system with eight protons, three of which are olefinic. The methylene protons in the remaining two propynyl groups are no longer equivalent and give rise to two slightly different AB-spin systems. The NMR spectrum is as expected for the norbornadiene derivative 3a, formed by an intramolecular Diels-Alder addition of one of the triple bonds to the cyclopentadiene ring in the 1-isomer of the ortho ester [NMR ($CDCl_3$, 270 MHz): δ 6.94 (H_5, dd, J 5.2 and 0.4 Hz), 6.84 (H_6, dd, J 5.2 and 3.1 Hz), 6.13 (H_2, broad q, J 2.4 Hz), 4.64 (H_3 or H_4, dd, J 14 and 2.0 Hz), 4.50 (H_3 or H_4, dd, J 14 and 2.4 Hz), 4.37 and 4.30 (2 H, splitted AB system, J 16 and 2.4 Hz), 4.34 and 4.30 (2 H, splitted AB-system, J 15.5 and 2.4 Hz), 3.84 (H_1, m), 2.44 (1 H, t, J 2.4 Hz), 2.40 (1 H, t, J 2.4 Hz), 2.36 (H_7 or H_8, dd, J 5.9 and 1.4 Hz), and 2.11 (H_7 or H_8, dd, J 5.9 and 1.5 Hz). MS (60 eV): m/e 242 (0.2 %, M^+), 241 (0.5), 203 (2.2), 187 (40), 157 (20), 148 (24), 147 (59), 141 (25), 131 (21), 129 (56), 128 (25), 104 (100), 103 (58), and 91 (60). Abs. mass 242.094; calc. for $C_{15}H_{14}O_3$ 242.095.]



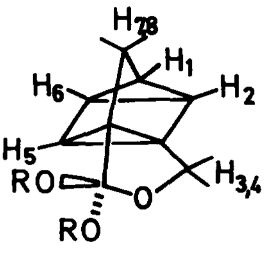
3a



3b



3c



4

R = $-CH_2-C\equiv CH$

In this case the intramolecular Diels-Alder addition is faster than the more common dimerisation and occurs exclusively in the 1-isomer of the cyclopentadieneorthocarboxylate. Inspection of molecular models (CPK) reveals that the products from the intramolecular Diels-Alder reactions in the 2- and 5-isomers of the ortho ester, compounds 3b and 3c, respectively, are severely strained and thus unlikely.

The structure of the norbornadiene derivative 3a was furhter proved by converting it to a quadricyclane derivative 4 by irradiation with light from a low-pressure mercury lamp in a Rayonet reactor with cyclohexane as solvent [65 % yield. NMR ($CDCl_3$, 270 MHz): δ 4.31 (2 H, d, *J* 2.5 Hz), 4.28 (1 H, dd, *J* 16 and 2.5 Hz), 4.23 (1 H, dd, *J* 16 and 2.5 Hz), 3.98 (H_3 or H_4, broad d, *J* 8.6 Hz), 3.81 (H_3 or H_4, broad d, *J* 8.6 Hz), 2.44 (H_6, dd, *J* 11.2 and 0.6 Hz) 2.39 (1 H, t, *J* 2.5 Hz), 2.38 (1 H, t, *J* 2.5 Hz), 2.14 (H_2, broad s), 2.12 (H_5, d, *J* 11.2 Hz), 1.78 (H_7 and H_8, m), and 1.64 (H_1, broad t, *J* 4.5 Hz). MS (60 eV): *m/e* 242 (0.05 %, M^+), 241 (0.2), 203 (0.4), 187 (12), 147 (18), 141 (13), 129 (24), 128 (22), 119 (25), 104 (64), 103 (65), 91 (83), 78 (49), 77 (35), 65 (47), 55 (25), and 39 (100)].

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