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Claisen Rearrangements of 6-Allyloxyfulvenes

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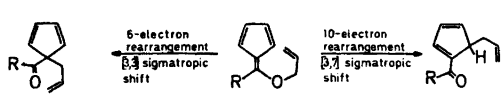
Trifluoromethylcyclopentadiene, potassium hydroxide and allyl alcohol give allyl 5-allylcyclopentadiene-5-carboxylate, *1*, by a Claisen rearrangement of the intermediately-formed 6-allyloxyfulvene. The analogous reaction with *cis*-2-butene-1,4-diol gives both a fulvene with an exocyclic ring, 2-cyclopentadienylidene-1,3-dioxacycloheptа-5-ene, *6*, and a *spiro* lactone from a Claisen rearrangement, 3-vinyl-γ-butyrolactone-2-*spiro*-5′-cyclopentadiene, *7*. When trifluoromethylcyclopentadiene is reacted with furfuryl alcohol and base, the reaction proceeds further *via* a Cope rearrangement and [1,5] sigmatropic shifts to yield 2-furanylmethyl ester of (2-furanylmethyl)cyclopentadiene carboxylic acid, *4*. The scope and limitations of these rearrangements are discussed as well as the two possible Claisen rearrangements of 6-allyloxyfulvenes, a 6 π- or a 10 π-electron sigmatropic reaction.

The Claisen rearrangement is one of the synthetically very useful reactions, whose mechanism has been understood only since the development of the theory of orbital-controlled concerted reactions.[1] Numerous examples of successful Claisen rearrangements of allyl aryl ethers and allyl vinyl ethers have been reported.[2]

We have recently prepared 6,6-dialkoxyfulvenes from trifluoromethylcyclopentadiene, an alcohol and base.[3] This method can be adopted easily for the preparation of 6-allyloxyfulvenes. Such compounds allow a comparison between competing 6 π- and 10 π-electron Claisen rearrangements, *i.e.* [3,3] and [3,7] sigmatropic reactions (Scheme 1). In this paper we report the synthesis and rearrangement of some 6-allyloxyfulvenes.



Scheme 1.

RESULTS AND DISCUSSION

When an ether solution of trifluoromethylcyclopentadiene is added to potassium hydroxide in allyl alcohol, allyl 5-allylcyclopentadiene-5-carboxylate, *1*, is formed in high yield. The product is formed by a Claisen rearrangement of either 6-fluoro-6-allyloxyfulvene followed by esterification of the acyl fluoride, or by rearrangement of 6,6-diallyloxyfulvene. Both reactions are possible and the course of the reaction is determined by the base concentration. The reaction can easily be followed by UV-spectroscopy (The different UV spectra of fluoro-oxy-fulvenes and dioxyfulvenes are shown in Ref. 3). When two equivalents of allyl alcoholate are added to trifluoromethylcyclopentadiene in ether, this procedure gives fluoro-oxy-fulvenes with aliphatic alcohols,[3] only a weak shoulder is observed at *ca* 278 nm and even this has completely disappeared within five min. However, a new band at 247 nm rises within one min. This band probably originates from the acyl fluoride. If, however five equivalents of allyl alcoholate are added, a strong absorption at 292 nm, indicating the presence of a 6,6-dioxyfulvene, develops. The absorption disappears only slowly (half life *ca* five min) and instead, a band at 254 nm, from the ester *1*, rises (Scheme 2).

A reasonable explanation for this observation is that the Claisen rearrangement of the fluoro-allyloxyfulvene is faster than that of the

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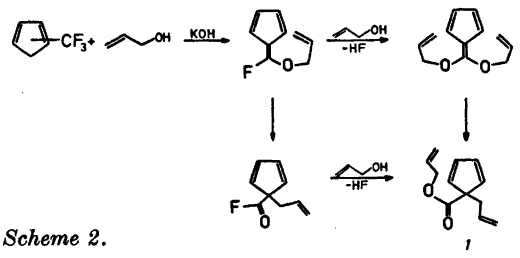
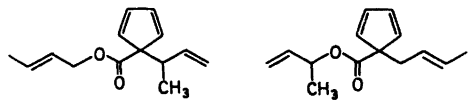
diallyloxyfulvene, but in the presence of excess base, the substitution of the last fluorine is even faster than the Claisen rearrangement.



Scheme 2.

The slower rearrangement of the dioxyfulvene compared to that of the fluoro-oxy-fulvene can be rationalized by examining the orbitals involved. The major primary interactions in the rearrangement should be between LUMO in the fulvene part (at C5) and HOMO of the allyl group. This is in agreement with CNDO calculations of the HOMO and LUMO energies of the fulvene, which give a smaller energy difference between HOMO(allyl) and LUMO (fulvene) than between LUMO(allyl) and HOMO(fulvene). Furthermore, the HOMO coefficients at C5 and C6 of the fulvene are small giving a poor interaction in the opposite direction. Increasing the electron-donating ability of substituents at the fulvene C6 increases the energy of the fulvene LUMO which decreases the interaction with the allyl HOMO and thus decreases the rate of the rearrangement.[4] This is further demonstrated by the observation that the more polarized 6-allyloxy-6-piperidinofulvene does not rearrange at room temperature.

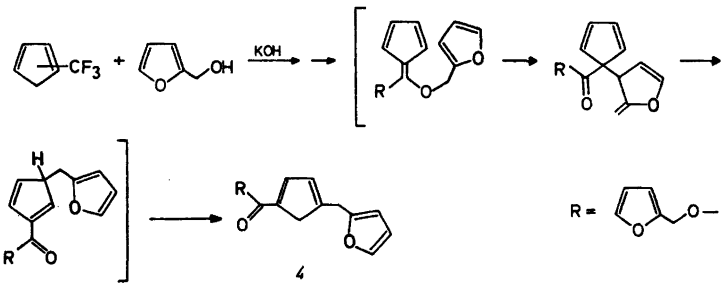
The concerted nature of the rearrangement is verified by reacting trifluoromethylcyclopentadiene with two methyl-substituted allyl alcohols, *trans*-2-butene-1-ol and 1-butene-3-ol. In both cases the expected product from a normal Claisen rearrangement, *trans* 2-butenyl 5-(1-methyl-2-propenyl)-cyclopentadiene-5-carboxylate, *2*, and 1-methyl-2-propenyl 5-(2-butenyl)cyclopentadiene-5-carboxylate, *3*, are isolated as the main products. The product from 1-butene-3-ol is mainly the *trans* isomer (NMR shows less than 5 % *cis* isomer). This is consistent with an equatorial position of the methyl substituent in a chair-like transition state, which is predicted from secondary interactions of the frontier orbitals.[5a]



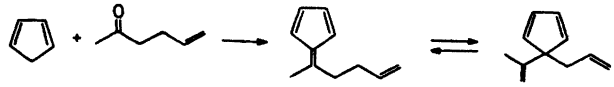
2 *3*

In contrast to other esters of cyclopentadienecarboxylic acid, allyl 5-allylcyclopentadiene-5-carboxylates are stable as monomers. Cyclopentadienecarboxylic acid esters dimerize as 1- and 2-isomers, in which the carbonyl group is conjugated with the five-membered ring.[6] This conjugation is essential for rapid dimerisation, as can be rationalized from frontier orbital theory.[5b] In the 5,5-disubstituted cyclopentadienes there is no such conjugation and no sigmatropic hydrogen shift, giving the 1- or 2-isomers, is possible and these esters are thus rather stable.

5-Allylcyclopentadienes could react further and undergo Cope rearrangements followed by sigmatropic hydrogen shifts to give a mixture of products. However, no such further rearrangements were observed with ordinary allyl groups. The only case in which a Cope rearrangement followed the Claisen rearrangement was when the allyl substituent was a rearranged furfuryl group (Scheme 3). In this very special case, the gain of resonance energy



Scheme 3.



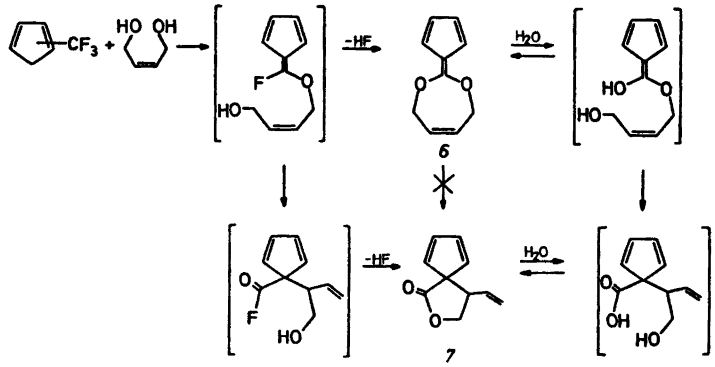
Scheme 4. 5

by reforming the furan ring strongly favours a subsequent Cope rearrangement. Subsequent Claisen and Cope rearrangements of furfuryl ethers have been observed by other workers.[7]

To investigate the corresponding Cope rearrangement of fulvenes, we prepared 6-methyl-6-(3-butenyl)fulvene, *5*, from cyclopentadiene and 5-hexen-2-one. The fulvene is rather stable, and no product from a Cope rearrangement was observed on heating the fulvene. Apparently, the loss of resonance energy of the fulvene on rearrangement forces the equilibrium in Scheme 4 to the left. In the Claisen rearrangement, the loss of the resonance energy in the 6,6-dioxyfulvene is more than compensated by the gain in bond and resonance energies in the ester formed.

The rapid Claisen rearrangement of all the 6,6-diallyloxyfulvenes studied made us look for a more stable 6,6-diallyloxyfulvene, in which the allyl groups were locked in a ring. *cis*-2-Butene-1,4-diol was reacted with trifluoromethylcyclopentadiene and base in the usual way. A rather unstable fulvene, 2-cyclopentadienylidene-1,3-dioxacyclohepta-5-ene, *6*, and a smaller amount of a *spiro* lactone, 3-vinyl-γ-butyrolactone-2-*spiro*-5′-cyclopentadiene, *7*, were both isolated from the reaction mixture (Scheme 5). The relative amounts of the two products varied with reaction conditions, which is consistent with the observation that the Claisen rearrangement can occur both before and after the substitution of the last fluorine. On heating, neither the fulvene nor the lactone rearranged. However, on prolonged contact with silica gel, probably containing some water, the fulvene slowly rearranges to the lactone. This probably occurs *via* a ring-opened intermediate as shown in Scheme 5.

The Claisen rearrangement is classified as a suprafacial, [3,3] sigmatropic shift which is symmetry allowed in the ground state. In 6-allyloxyfulvenes, another thermally allowed rearrangement, a suprafacial, [3,7] sigmatropic shift would also be possible (Scheme 1). Geometrically there is no major energy difference between the two reactions, and the [3,7] shift should lead to a thermodynamically somewhat more stable product. However, experimental results show that the [3,3] shift is the dominant reaction. No product from the [3,7] shift has been observed, and the reason for this must lie in the different electronic structures of the two transition states. Both reactions proceed *via* an "aromatic" intermediate (6 π- or 10 π-electrons), but the transition state of the [3,7] shift is azulene-like and the resonance energy in azulene is known to be less than in the benzenoid aromatics.[8] This thus leads to a higher energy of activation for the [3,7] shift than for the [3,3] shift.



Scheme 5.

EXPERIMENTAL

UV spectra were recorded on a Beckman DK 2A, NMR spectra on a Bruker WH 270, IR spectra on a Beckman IR 9 and mass spectra on an AEI MS 902 instrument.

Allyl 5-allylcyclopentadiene-5-carboxylate. A solution of potassium hydroxide in allyl alcohol (25 ml, 0.5 M) was slowly added to an ether solution of trifluoromethylcyclopentadiene [3] (25 ml, 0.15 M). After 15 min at room temperature the reaction mixture was washed with several portions of water to remove excess allyl alcohol and potassium salts. The solvent was evaporated and the residue was purified by chromatography on silica gel with chloroform as eluent to give allyl 5-allylcyclopentadiene-5-carboxylate (0.67 g, 94 %). NMR ($CDCl_3$): δ 6.35–6.45 (4 H, AA'BB' pattern) cyclopentadienyl protons, 5.87 (1 H, ddt, J 17, 10 and 5 Hz), 5.26 (1 H, dq, J 17 and 1.5 Hz), 5.19 (1 H, dq, J 10 and 1.5 Hz), 4.54 (2 H, dt, J 5 and 1.5 Hz) allyl ester group, 5.71 (1 H, ddt, J 17, 10 and 7 Hz), 5.08 (1 H, broad dd, J 17 and 2 Hz), 5.02 (1 H, broad dd, J 10 and 2 Hz) and 2.58 (2 H, d, J 7 Hz) allyl group. IR: 1730, 1220, 780 and 720 cm^{-1}.[9] UV(ethanol): λ_{max} 254 nm, log ε 3.06. MS (70 eV): m/e 190 (10 %, M^+), 149 (70, $M^+ - C_3H_5$), 105 (100, $M^+ - C_3H_5 - CO_2$), 79 (64) and 41 (94).

trans-*2-Butenyl 5-(1-methyl-2-propenyl)cyclopentadiene-5-carboxylate* was prepared from *trans*-2-butene-1-ol and trifluoromethylcyclopentadiene as described above. Yield 472 mg (90 %). NMR($CDCl_3$): δ 6.33–6.40 (4 H, disturbed AA'BB' pattern) cyclopentadienyl protons, 5.73 (1 H, dqt, J 16, 6.5 and 1.0 Hz), 5.54 (1 H, dtq, J 16, 6 and 1.5 Hz), 4.47 (2 H, dm, J 6 and 1.0 Hz), and 1.70 (3 H, dm, J 6.5 and 1.5 Hz) 2-butenyl ester group, 5.64 (1 H, ddd, J 17, 10.5 and 7 Hz), 5.01 (1 H, ddd, J 17, 1.5 and 1.0 Hz), 4.94 (1 H, ddd, J 10.5, 1.5 and 1.0 Hz), 3.04 (1 H, quintet of triplets, J 7 and 1.0 Hz) and 0.99 (3 H, d, J 7 Hz) 1-methyl-2-propenyl group. The assignment and coupling constants were confirmed by several decouplings. MS(70 eV): m/e 218 (5 %, M^+), 163 (11, $M^+ - C_4H_7$), 119 (17, $M^+ - C_4H_7 - CO_2$), 117 (11), 91 (16), 72 (13) and 55 (100). Abs. mass: 218.131; calc. for $C_{14}H_{18}O_2$: 218.131.

1-Methyl-2-propenyl 5-(2-butenyl)cyclopentadiene-5-carboxylate was prepared from 1-butene-3-ol and trifluoromethylcyclopentadiene as described above. Yield 193 mg (37 %). NMR ($CDCl_3$): δ 6.30–6.45 (4 H, AA'BB' pattern) cyclopentadienyl protons, 5.80 (1 H, ddd, J 17, 10.5 and 5.5 Hz), 5.31 (1 H, m, J 6.5, 5.5 and 1.3 Hz), 5.20 (1 H, dt, J 17.0 and 1.3 Hz), 5.10 (1 H, dt, J 10.5 and 1.3 Hz), and 1.27 (1 H, d, J 6.5 Hz) 1-methyl-2-propenyl ester, 5.51 (1 H, dqt, J 15.0, 6.0 and 1.0 Hz), 5.37 (1 H, dtq, J 15.0, 7.0 and 1.5 Hz), 2.48 (1 H, broad d, J 7 Hz), 1.62 (1 H, dm, J 6.0 Hz) 2-butenyl group. The assignment and coupling constants were confirmed by several decouplings. MS (70 eV): m/e 218 (7 %, M^+), 163 (14, $M^+ - C_4H_7$), 119 (24, $M^+ - C_4H_7 - CO_2$), 117 (21), 91 (27), 79 (54), 55 (100). The coupling constants in the 2-butenyl group show that only the *trans* isomer has been formed.

2-Furanylmethyl ester of (2-furanylmethyl)-cyclopentadiene carboxylic acid was prepared from furfuryl alcohol and trifluoromethylcyclopentadiene as described above. The product was isolated from undefined polymeric material by HPLC on silica gel with methylene chloride as eluent. Yield 65 mg (15 %). NMR($CDCl_3$): δ 7.41 (1 H, dd, J 1.7 and 1.0 Hz), 6.42 (1 H, broad d, J 3 Hz), 6.36 (1 H, dd, J 3 and 1.7 Hz) and 5.15 (2 H, s) furfuryl ester group, 7.31 (1 H, dd, J 1.8 and 1.0 Hz), 6.29 (1 H, m), 6.04 (1 H, disturbed d, J 3 Hz) and 3.77 (2 H, s) furfuryl group, 7.34 (1 H, m), 6.28 (1 H, m) and 3.27 (2 H, dd, J 1.5 and 1.1 Hz) cyclopentadiene protons. The assignment was made by several decouplings. These also show that the coupling constant between the two olefinic cyclopentadiene protons is 2.0 Hz which indicates that the cyclopentadiene is substituted in the 1- and 4- positions.[10] Other isomers are also present in small quantities in the equilibrium mixture as shown in the NMR spectrum. MS (70 eV): m/e 270 (13 %, M^+), 189 (5, $M^+ - C_5H_5O$), 173 (15, $M^+ - C_5H_5O_2$), 81 (100). Abs. mass: 270.089; calc. for $C_{16}H_{14}O_4$: 270.089.

6-Methyl-6-(3-butenyl)fulvene. 5-Hexen-2-one (20 g) and freshly distilled cyclopentadiene (14 g) were dissolved in 150 ml methanol. Propylamine (3 ml) was added and the solution was refluxed 48 h. The product was separated from unreacted ketone and cyclopentadiene dimer by distillation. Yield 15.5 g (52 %) b.p. 97 °C at 15 Torr. NMR($CDCl_3$): δ 6.40–6.50 (4 H, m) ring protons, 5.78 (1 H, ddt, J 17, 10, and 6.7 Hz), 5.03 (1 H, dq, J 17 and 1.7 Hz), 4.96 (1 H, ddt, J 10, 1.8 and 1.2 Hz), 2.57 (2 H, t, J 7.8 Hz) and 2.27 (2 H, m) butenyl group, 2.14 (3 H, s) methyl group. UV(ethanol): λ_{max} 271 nm, log ε 4.26, 356 nm, log ε 2.56.

6-Allyloxy-6-piperidinofulvene was prepared from 6-fluoro-6-piperidinofulvene [3] and allyl alcoholate. NMR($CDCl_3$): δ 6.47 (2 H) and 6.31 (2 H) AA'BB' pattern, five-membered ring protons, 6.01 (1 H, ddt, J 17, 10, and 6 Hz), 5.39 (1 H, dq, J 17 and 1.3 Hz), 5.31 (1 H, dq, J 10 and 1.3 Hz) and 4.90 (2 H, dt, J 6 and 1.3 Hz) allyl ether group, 3.74 (4 H, broad) and 1.71 (6 H, broad) piperidine protons.

2-Cyclopentadienylidene-1,3-dioxocycloheptа-5-ene, and *3-vinyl-γ-butyrolactone-2-spiro-5'-cyclopentadiene. cis*-2-Butene-1,4-diol (1.05 g, 12 mmol) was dissolved in dry diethyl ether. Butyl lithium in hexane (6 ml, 1.5 M) was added and the slurry was cooled to −35 °C. A solution of trifluoromethylcyclopentadiene in ether (10 ml, 0.1 M) was added and the slurry was stirred for 2 min. The reaction was stopped by adding large amounts of water and the ether layer was washed with several portions of

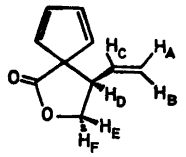


Fig. 1. The lactone *7*.

water, dried over sodium sulfate and the solvent evaporated. The crude product contained the fulvene, *6*, and the lactone, *7*, in an 8:1 ratio. The total yield was 151 mg (92 %). Separation of the two products by chromatography on silica gel led to a large and varying decrease in the yield of pure fulvene while the yield of pure lactone could be raised to *ca.* 30 %.

Fulvene: NMR($CDCl_3$): δ 6.55 (2 H) and 6.21 (2 H) AA'BB' pattern, five-membered ring protons, 5.80 (2 H, t) and 4.74 (4 H, d, J 1.8 Hz). UV (hexane): λ_{max} 288 nm. MS (70 eV): *m/e* 162 (19 %, M^+), 132 (42, $M^+ - CH_2O$), 104 (100, $M^+ - C_2H_2O_2$), 103 (34), 78 (37) and 77 (31).

Lactone. NMR ($CDCl_3$): δ 6.63 (1 H, m), 6.57 (1 H, m), 6.38 (2 H, m) 5.57 (1 H, m, H_C), 5.10 (1 H, dt, H_A), 5.08 (1 H, dt, H_B), 4.60 (1 H, dd, H_E), 4.28 (1 H, t, H_F) and 3.62 (1 H, broad q, H_D), J_{AB} 1.0 Hz, J_{AC} 10 Hz, J_{AD} 1.0 Hz, J_{BC} 17 Hz, J_{BD} 1.0 Hz, J_{CD} 7 Hz, J_{DE} 7.5 Hz, J_{DF} 9 Hz and J_{EF} 9 Hz. The assignment and coupling constants were confirmed by selective decoupling of all protons H_A to H_F (see Fig. 1). MS (70 eV): *m/e* 162 (26 %, M^+), 132 (50, $M^+ - CH_2O$), 117 (58), 104 (100, $M^+ - C_2H_2O_2$), 103 (42), 78 (29) and 77 (27). Abs. mass: 162.069; calc. for $C_{10}H_{10}O_2$: 162.068.

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