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CYCLOADDITIONS OF 6-SILYLOXYFULVENES : ACCESS TO 7-NORBORN-5-ENYL AND 7-NORBORNA-2,5-DIENYLALDEHYDES AND KETONES

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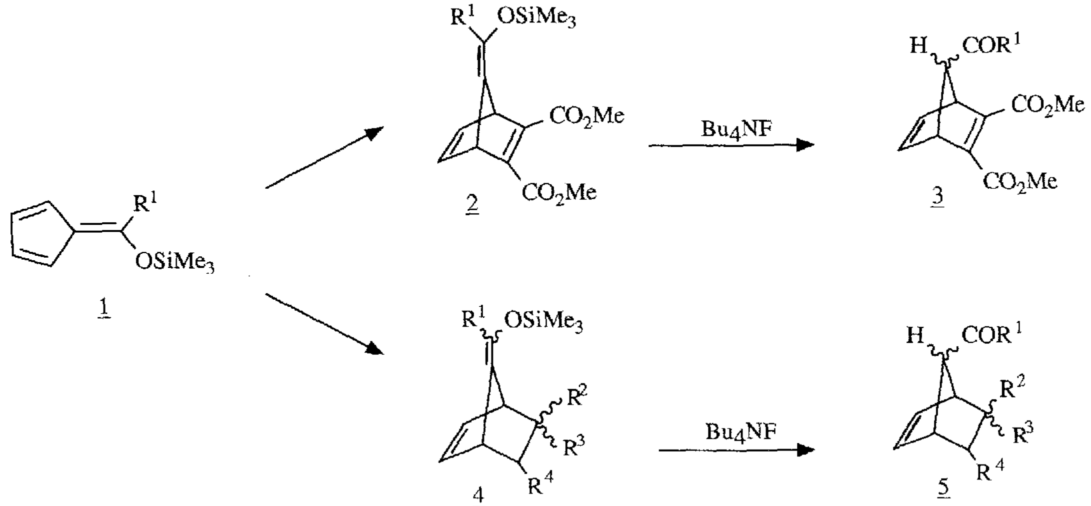
Summary. Reactions of 6-silyloxy-6-alkyl-fulvenes with dimethyl acetylenedicarboxylate, maleic anhydride and 2-chloroacrylonitrile resulted in the formation of expected 7-substituted bicyclo [2.2.1]hepta-2,5-diene and hept-5-ene derivatives. Treatment of these adducts with Bu_4NF produced the 7-norborn-5-enyl and 7-norborno-2,5-dienyl aldehydes and ketones in good yields.

Preparations of unsaturated 7-substituted bicyclo [2.2.1]heptane derivatives are of interest, such compounds being useful intermediates (1) in organic synthesis. [4+2] cycloadditions of 1-acyl or 1-methoxy -carbonyl-2,4-cyclopentadiene with various dienophiles could be a good route to these derivatives. However these dienes give unsaturated 5-substituted bicyclo [2.2.1] heptenes because of the rapid isomerization of the starting materials (2) in thermodynamically more stable 1-substituted-1,3-cyclopentadienes. [4+2] cyclo -additions of 6-heterosubstituted fulvenes (3) or nickel (4) or iron (5) derivatives of cyclopentadiene are of better use as it has been recently shown. Silyl enol ethers being very useful intermediates in organic synthesis (6) we thought it could be interesting to prepare and use 6-silyloxy-6-alkyl fulvenes as synthons for an easy access to 7-norborn-5-enyl and 7-norborna-2,5-dienyl aldehydes and ketones.

Sodium formyl-, acetyl-, butyryl-, or isobutyrylcyclopentadienide can be obtained easily from the known coupling of sodium cyclopentadienide with methyl formate, acetate, butyrate or isobutyrate (7). We found that the condensation of these sodium salts with Me_3SiCl or $tBuMe_2SiCl$ gave the wanted 6-silyloxy-6-alkyl fulvenes 1, whereas the same condensation with Me_3SnCl or Bu_3SnCl led to unstable ring-stannylated products.

The substituted silyloxyfulvenes 1 were isolated as highly polymerisable oils after filtration and evaporation of the solvent. An increase of the substitution of R^1 (R^1=iPr or tBu) or the use of an aryl group (R^1=Ph) resulted in a severe drop of the yield in 1 (R^1(%) : H(91), Me(94), Et(70), nPr(62), iPr(10), tBu(0), Ph(0)). The 6-silyloxy-6-alkylfulvenes 1 were next reacted with dimethyl acetylenedicarboxylate, maleic anhydride and chloroacrylonitrile to give adducts 2 and 4, easily transformed in the epimeric 3 or 5 (8)(9)(10) after treatment with a THF solution of Bu_4NF.

The method proposed here brings up an improvement of the use of 6-methyl-6-methoxyfulvene which adducts give isomeric ethers instead of the expected ketones (3) when they are treated under hydrolysis conditions. In our case the more labile silicon-oxygen bond was cleaved without difficulty to lead to the wanted carbonylated compounds. It also provides an easy access to reactive adducts 2 and 4 susceptible of interesting developments.



R^1	R^2	R^3	R^4	2(%)	3(%)	4(%)	5(%)
H				89	37		
Me				63	74		
iPr				75	80		
H	Cl(CN)	CN(Cl)	H			78	45
H	H	COOCO				70	52
Me	Cl(CN)	CN(Cl)	H			80	48
Me	H	COOCO				94	64
nPr	Cl(CN)	CN(Cl)	H			86	58

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8- The preparation of 3 (R^1=Me) is representative. To a suspension of 5.8g (50 mmol) of sodium acetylcyclopentadienide (R^1=Me) in 100 ml of anhydrous diethylether at 0°C under nitrogen, was slowly added 6.4g (60 mmol) of Me_3SiCl. After one hour the suspension was filtered and the solvent evaporated. Crude 1 (R^1=Me) in 25 ml of dry toluene was then reacted with 8.5g (60 mmol) of dimethyl acetylenedicarboxylate at 80°C during 24 hours. After evaporation of the solvent the residue was chromatographed on Florisil (pentane/acetone : 90/10).^{1}H NMR : (ppm) (CCl_4) : 0.12 (s, 9H) 1.61 (s, 3H) 3.67 (s, 6H) 4.15 (m, 1H) 4.35(m, 1H) 6.92 (m, 2H). The adduct (2g, 6.2 mmol) in 10 ml of dry THF at 0°C was treated by 6.5 ml of a 1 M solution of TBAF in THF during 30 mn. After hydrolysis with a saturated solution of NH_4Cl, diethylether extraction and evaporation of the solvent, the residue was chromatographed on Florisil (pentane:acetone : 90/10) and recovered as a mixture of epimers (45/55) 3 (R^1=Me) ^{1}H NMR (ppm) (CCl_4) : 1.90 and 2.02 (s, 3H) 3.10 and 3.28 (m, 1H) 3.70 (s, 6H) 4.13 (m, 2H) 6.68 and 6.81 (m, 2H).

9- Compounds 3 and 5 are obtained as equimolecular mixture of epimers. We did not try to separate them. They give correct ^{1}H NMR, IR, mass spectrometry data.

10- Isolated, purified yields.

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