

TITANIUM-INDUCED CONJUGATE ADDITION  
OF THE FLUORENONE DIANION TO  $\alpha,\beta$ -ENONES

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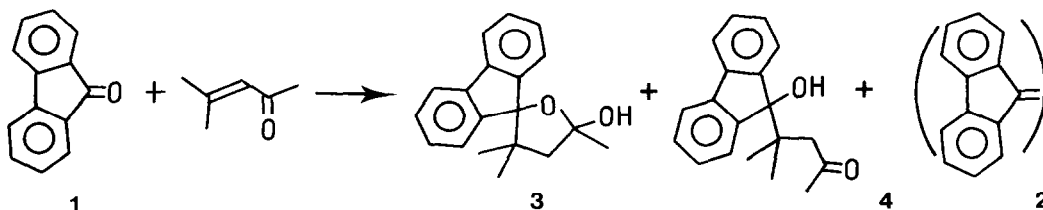
Summary Cross-coupling of fluorenone and enones with  $TiCl_4$ -Mg led to  $\gamma$ -ketol derivatives resulting of a conjugate addition of the fluorenone dianion to enones.

During the past decade, the chemistry of the titanium-induced reductive coupling of ketones to diols or olefins has received considerable attention (1)

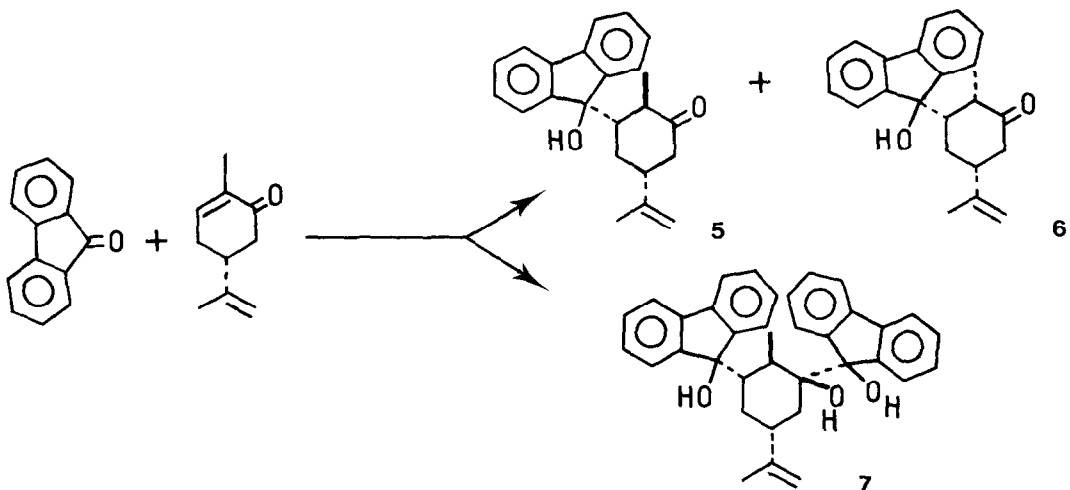
Our interest has recently been focused on the reactivity of  $\alpha,\beta$ -enones (2) This communication summarizes some of our observations in the area of mixed coupling between fluorenone and aliphatic enones Early works with titanium reagents and aliphatic saturated ketones (3) or diarylketones and dialkylketones (4) shown that amounts of the crossed olefins were somewhat greater than the statistical value.

The cross coupling is performed by stirring at room temperature a 1-1 mixture of fluorenone 1 and enones with  $TiCl_4$ -Mg reagent ( 2 equivalents )(2) in THF under a nitrogen atmosphere for 24 h

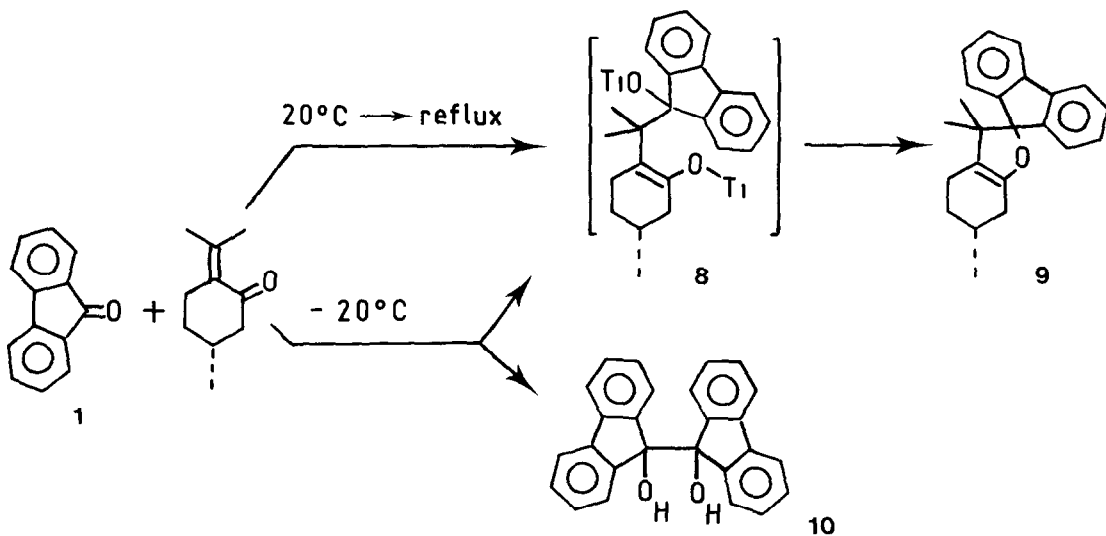
Reaction of fluorenone with mesityl oxide and column chromatography of the resulting product mixture led to the isolation of bifluorenylidene 2 ( 5 % ), 3 ( 70 % )(5) and 4 ( 25 % )(6). Product mixture contains less than 3 % ( if any ) of the self-coupled products of mesityl oxide (2)



Condensation of fluorenone with (R)-(-)-carvone gave the conjugate addition products 5 ( 70 % )(7), 6 ( 5 % )(8), 7 ( 10 % )(9) and 2 ( 5 % )(with 10 % of unreacted carvone )



Treatment of (R)-(+)-pulegone and fluorenone with  $TiCl_4$ -Mg and refluxing ( 0 5 h ), effected the elimination of titanium oxide species from the intermediate enolate 8 giving the enol ether 9 ( 96 % )(10)

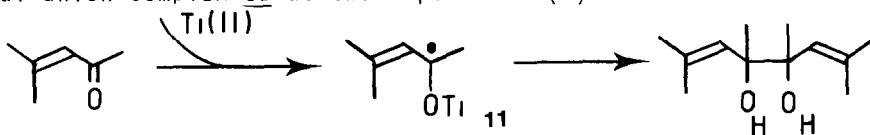


Even when the above reaction was carried out at low temperature (  $-20^\circ C$  ), the enol ether 9 was the major product ( 70 % ), with slight formation of bis-fluorenone 10 ( 10 % )

Discussion Three processes can be involved to explain  $\gamma$ -ketols formation

\* Condensation of fluorenone and enones radical anions

Our preliminary results are in agreement with a highest spin density of the radical anion complex 11 at the 2-position (2)



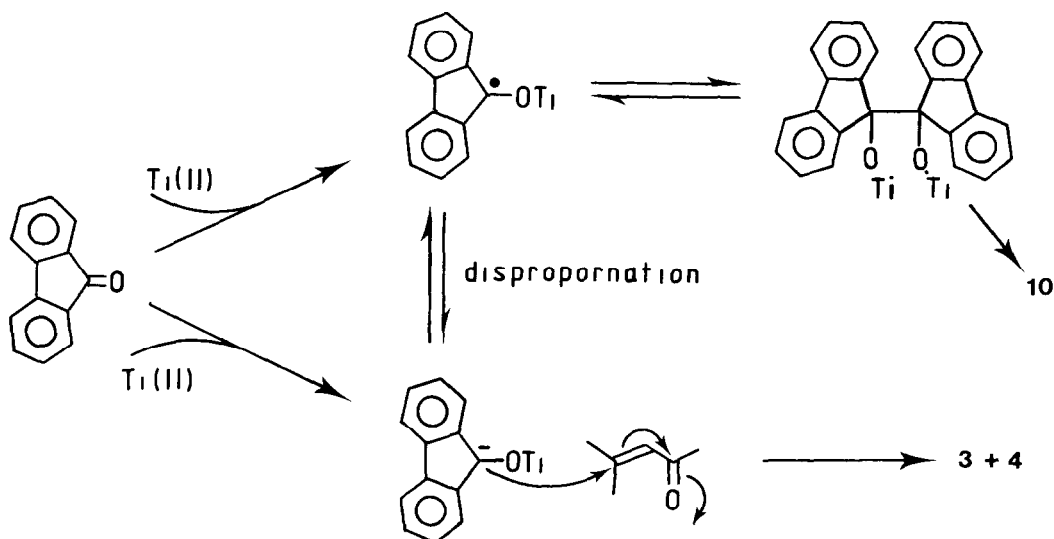
Therefore, the condensation of the radical 11 with the fluorenone radical anion should lead to a diol

\* Conjugate addition of the fluorenone radical anion to enones

The radical anion of fluorenone has been observed by ESR measurements in similar reaction (11). But by analogy with other aromatic radicals (12), addition of the radical anion of fluorenone should occur at the  $\alpha$  and  $\beta$  positions of the enones.

\* Conjugate addition of the fluorenone dianion to enones

The structure of addition products suggests the formation of the fluorenone dianion, resulting from the further reduction of the radical anion by  $Ti(II)$  species (or from disproportionation equilibrium of the radical anion with the dianion and the neutral molecule (13)), followed by conjugate addition to enones (14). The fluorenone dianion structure is expected to give such 1,4-additions (15). It should be pointed out that the anion radical originally produced exists with its dimer, but the latter serves as a reservoir for the reactive monomer (16).



References and notes :

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- 5 3 : m.p. 113 °C; HRMS found 280.1461, calcd 280.146320 for C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>;  
ir ( CCl<sub>4</sub> ) : 3410, 1380, 1295, 1180, 1100, 1010, 940, 905 cm<sup>-1</sup>.
- 6 4 : ir ( CCl<sub>4</sub> ) : 3425, 1725, 1610, 1380, 1300, 1185-1200, 1095, 1020, 920 cm<sup>-1</sup>.
- 7 5 : m.p. 242 °C; HRMS found 332.1774, calcd 332.177619 for C<sub>23</sub>H<sub>24</sub>O<sub>2</sub> ;  
ir ( CDCl<sub>3</sub> ) : 3550, 3420, 3040, 1720, 1645, 1375, 1260, 1020, 895 cm<sup>-1</sup>.
- 8 6 : m.p. 76 °C; ir ( CCl<sub>4</sub> ) : 3600, 3020, 1700, 1320, 1030, 1005, 905 cm<sup>-1</sup>.
- 9 7 : m.p. 236 °C; MS : 514 (1%), 496 (2%), 333 (8%), 315 (43%), 243 (46%),  
205 (23%), 191 (23%), 182 (75%), 181 (100%), 180 (59%), 165 (88%), 152 (54%);  
HRMS found 333.1852, calcd 333.185443 for C<sub>23</sub>H<sub>25</sub>O<sub>2</sub>; ir ( CDCl<sub>3</sub> ) : 3600,  
3010, 1960, 1920, 1640, 1610, 1370, 1290, 1180, 1020, 1000 cm<sup>-1</sup>.
- 10 9 : m.p. 101 °C; HRMS found 316.1834, calcd 316.182704 for C<sub>23</sub>H<sub>24</sub>O;  
ir ( CCl<sub>4</sub> ) : 1720, 1360, 1290, 1260, 1210, 1175, 1110, 990, 930 cm<sup>-1</sup>.
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( about -2.2 to -2.3 V *vs sce* (17) ).
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