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CONJUGATE ADDITION OF THE DIANION OF DIARYL KETONES TO α,β - ETHYLENIC KETONES PROMOTED BY $TiCl_4$-Mg.

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Abstract : Cross coupling of diaryl ketones and enones promoted by $TiCl_4$ -Mg leads to the formation of products involving a Michael -type addition; this 1,4- addition is on some occasions followed by cyclization yielding hemiacetals and/or dihydrofurans.
Résumé : Le couple $TiCl_4$-Mg réduit les diaryl cétones en dianions qui s'additionnent en 1,4 sur les α-énones pour conduire principalement à des γ-cétols qui peuvent se cycliser et conduire à des hémiacétals et/ou des dihydrofuranes.

The use of low valent titanium species to create new carbon-carbon bonds is now well established . Thus reductive dimerisation of aliphatic ketones leading to pinacols and/or alkenes has been extensively studied (1-3). Reactions of diaryl ketones have received less attention, but it is known that cross-coupling reactions (between diaryl ketones and aliphatic ketones) can be promoted by low valent titanium species (4,5) as well as by lanthanoid metal reagents (6). In the course of our study on the reactivity of α,β-ethylenic ketones promoted by the $TiCl_4$-Mg reagent (7), we now report on the conjugate addition of the fluorenone and xanthone dianions to α-enones; this addition is in some cases followed by a cyclization. A preliminary communication on part of this work has already been published (8).

Results.

The action of the $TiCl_4$-Mg/THF reducing system on an equimolar mixture of diaryl ketone 1 and enone 2 leads generally to adducts 3, 4 and 5 (scheme I); alongside these three types of products, compounds of different structure are occasionally formed (see table I and scheme II). The relative proportions of compounds 3, 4 and 5 depend both on the structure of the enone involved and on the reaction conditions (table I).

Scheme I

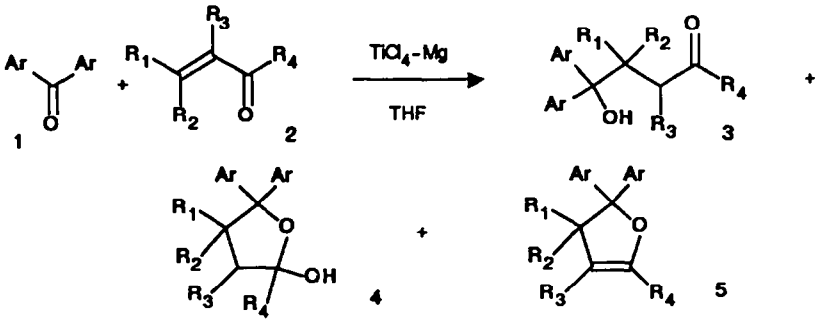


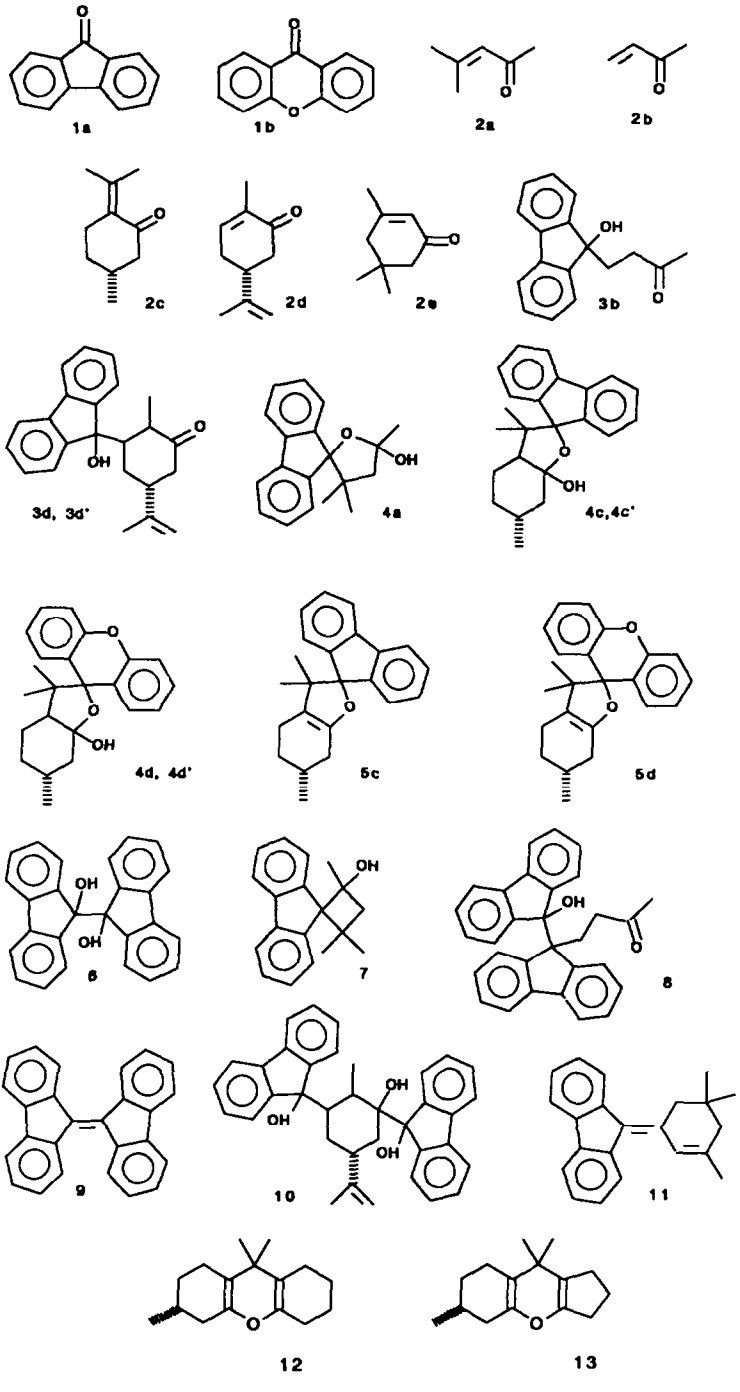
Table I : Coupling between diaryl ketones 1 and enones 2.

	Starting Materials		Reaction Conditions			Products			
Entry	Diarylketone	Enone	Reagents (ratio vs 1)	Temp.(°C)	Time (h)	Ketol	Hemiacetal	Enol ether	Others
1	1a	2a	$TiCl_4$-Mg(4)	0→ r.t.	7		4a (71%)		6 (6%)
2[a]	1a	2a	$TiCl_4$-Mg(2)	r.t.	4		4a (16%)		7(31%)
3	1a	2b	$TiCl_4$-Mg(2)	0 → r.t.	8	3b(32%)			8(53%)
4	1a	2b	$TiCl_4$-Mg(3)	35°C	2	3b(57%)			8 (8%)
5	1a	2c	$TiCl_4$-Mg(2)	r.t.	4			5c (63%)	
6	1a	2c	$TiCl_4$-Mg(3)	35°C	0.5		4c (24%) 4c' (34%)	5c (15%)	9(10%)
7[a]	1b	2c	$TiCl_4$-Mg(2)	20°C	24			5d (45%)	
8[a]	1b	2c	$TiCl_4$-Mg(3)	35°C	1		4d (12%) 4d' (23%)	5d (23%)	
9	1a	2d	$TiCl_4$-Mg(2)	r.t.	72	3d (5%) 3d' (60%)			10(10%)
10[a]	1a	2e	$TiCl_4$-Mg(4)	0 → r.t.	36				11(40%)

a) these conditions are the best for the obtention of the described compounds without too many side products; starting materials are recovered.

Adducts 3 are generally the initial products (isolated or not) of the reaction between diaryl ketones 1 and enones 2; hydrocarbon 11, obtained from fluorenone 1a and isophorone 2e, is the only example of adduct resulting from the carbonyl attack (entry 10).

Scheme II



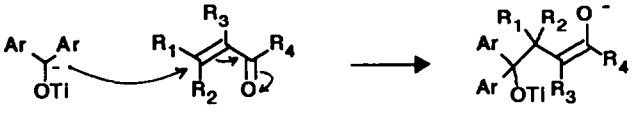
Thus, when the reaction is performed with methyl vinyl ketone **2b** (entry 4) or (-)-carvone **2d** (entry 9) and fluorenone **1a**, the main product is ketol **3b** or ketol **3d**. But with mesityl oxide **2a** (entry 1) and (+)-pulegone **2c** (entries 6 and 8), ketols are probably too unstable and they undergo cyclization leading to hemiacetals **4a,c,d**. However, in the case of (+)-pulegone **2c**, a rapid dehydration of hemiacetals **4c,d** yielding stable enol ethers **5c,d** can take place and an excess of reagent must be used to isolate hemiacetals **4c,d** (entry 6 *vs* entry 5 and entry 8 *vs* entry 7).

Finally, it is worth underlining the unusual structure of compounds **7** (entry 2) and **8** (entries 3 and 4).

Discussion.

Both the first (leading to the radical anion: $E_{1/2}$ = -1.29 V) and the second reduction potentials (leading to the dianion : $E_{1/2}$ = -1.95 V) of fluorenone **1a** are less negative than the reduction potential for the formation of the radical anion of the enone ($E_{1/2}$ = -2.3 to -2.4 V) (9); the fluorenyl dianion can, therefore, coexist with the enone. Moreover, apart from a very little amount of bifluorenol **6** (6%, entry 1), no symmetrical dimers of diaryl ketones or enones, resulting from a single-electron transfer pathway (10), are formed. A radical process can also be ruled out because, in spite of the various enones studied, no α-attack has ever been noticed (11). For all these reasons, we think that a 1,4-nucleophilic addition of the dianion of the diaryl ketone to the enone is the most likely mechanism (scheme III). Finally, the 1,4-nucleophilic addition is also supported by the structure of the dianion of fluorenone, which has some caracteristics known to promote 1,4 addition (12-14): well delocalized negative charge, several occupied orbitals and an sp_2-hybrided functional carbon.

Scheme III



Carbanionic intermediates have already been proposed by McMurry to explain the cross-coupling between diaryl ketones and aliphatic ketones (4) and work, by Walborsky in particular, has provided some confirmation to such a mechanism (15).

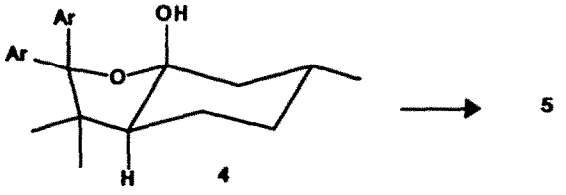
Since isophorone **2e** is known as a poor 1,4 acceptor (16)(because of the presence of a methyl group in an axial position), the formation of **11** (entry 10) is not surprising; thus, it can be explained by a 1,2 nucleophilic addition of the fluorenyl dianion on the isophorone **2e** followed by elimination.

When the 1,4-adduct **3** is formed, depending on different parameters, it can cyclize and yield **4** and even **5** after elimination. When cyclization is possible (**2a**,**2b** and **2c**), the presence of *gem*- dimethyl groups on the β carbon (**2a** and **2c**) seems to be an important factor; indeed, the repulsion between the two methyl groups provokes a widening of the angle between the bonds of the two other substituents (Thorpe-Ingold

effect) (17) which favors the cyclization. In the absence of *gem* - dimethyl substituents (**2b**), the process stops after the 1,4-addition.

Formation of enol ethers **5c** and **5d** under "standard" conditions may be due to their stability (at least when compared with hemiacetals **4c**, **4c'**, **4d** and **4d'**) or to the fact that the hydroxy group of the hemiacetals can exist in an axial position, *anti* with the bridgehead hydrogen atom, and therefore be in a favored position for elimination (scheme IV).

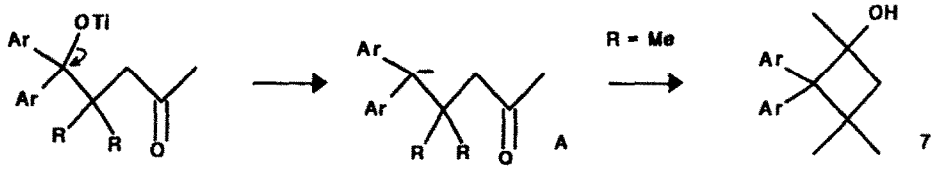
Scheme IV



The fact that 1,4-addition on (+)-pulegone leads predominantly to ethers is already known in the case of photochemical condensation of methanol (18-21); moreover, we have established that condensation of 1-trimethylsilyloxy cyclohexene and 1-trimethylsilyloxy cyclopentene on (+)-pulegone under Mukaiyama conditions (22) leads to cyclic enol ethers **12** and **13** (23) and not to the expected diketones.

Finally, the formation of **7** (entry 2) and **8** (entries 3 and 4) may result from the attack of the substituted fluorenyl carbanion **A** generated by the initial 1,4-condensation and a reductive loss of OTi generating a carbanionoid species. In the case of mesityl oxide **2a** (entry 2)(R = Me), the presence of the *gem* - dimethyl groups (17) favours *intra* molecular reaction leading to the spiro [3.4] octane **7** (scheme V).

Scheme V



With methyl vinyl ketone **2b** (entries 3 and 4), carbanion **A** (R = H) would condense on another molecule of fluorenone to form **8** because cyclization is no longer favoured by the presence of the *gem* - dimethyl groups.

Conclusion

The reactivity of diaryl ketones with enones shows the ability of the $TiCl_4$-Mg system to transfer two electrons. The 1,4 addition is a general reaction but the exact structure of the enone determines the eventual disposition of the ketol which can undergo various subsequent transformations.

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Experimental

General Methods. ^1H NMR spectra of $CDCl_3$ solutions were obtained on Brucker AC 200 (200 MHz), Varian XL 200 (200 MHz) and Cameca (250 MHz) spectrometers. ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Varian XL 200 (50.31 MHz) spectrometer with Me_4Si as the internal reference; attributions were confirmed by J-modulated spin echo techniques. Mass spectra were obtained on a Varian MAT 311 mass spectrometer. IR spectra were recorded on a Perkin-Elmer 298 spectrometer. Optical rotations were measured on a Perkin-Elmer 241 in a thermostated 10cm cell. Melting points are uncorrected. All reactions were carried out in an argon atmosphere and the additions done *via* a syringe.

Materials. The various reagents were obtained from Fluka AG (or Aldrich for (-)-carvone) and purified as usual. (+)-Pulegone was obtained, by distillation and chromatography on silica gel, from the oil of *Mentha Pulegenium* (Morocco) ($[\alpha]_{578}^{20}$ = +30.1°, c 2.24, hexane).

General Procedure for Reductive Cross Coupling of Enones and Diaryl Ketones Using $TiCl_4$-Mg : In a dry two-necked flask equipped with a magnetic stirrer, magnesium (Grignard turnings)(10 mmol., 0.243 g) was placed in anhydrous THF (10 ml). The reaction flask was cooled to -60 °C before $TiCl_4$ (10 mmol., 1.10 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature in 3-4 h. and the resulting black slurry was stirred for an additional 20 h. A solution of enone and diaryl ketone (2.5, 3.3 or 5 mmol. of each as indicated in Table I) in 2 ml of THF was added dropwise and the reaction mixture was stirred (time and temperature are indicated in Table I) until it was poured into ice-ammonium chloride solution. After the usual extractive work-up procedure with diethyl ether, the organic layer was washed with brine, dried over magnesium sulphate and concentrated under reduced pressure. Finally, the products of the reaction were isolated by chromatography on silica gel and if solids purified by crystallization.

Reductive Cross Coupling of Fluorenone 1a and Mesityl Oxide 2a.

Preparation of hemiacetal 4a and bifluorenol 6 (24). Table I, entry 1: 2.5 mmol. (0.450 g) of 1a and 2.5 mmol. (0.245 g) of 2a were used; the addition was done at 0 °C before temperature was allowed to warm to room

temperature over 2 h.; stirring was continued at room temperature for an additional 5 h. Products **4a** (71%) and **6** (6%) were isolated by flash chromatography (ether-pentane : 12-88 and 20-80). **Hemiacetal 4a** : mp 122 °C (CCl_4); IR (CCl_4) 3410, 1295, 1180, 1100, 1010, 940, 905 cm^{-1}; ^1H NMR (200 MHz) d 7.90 (1, d, J = 7.0 Hz), 7.56 (2, d, J = 6.0 Hz), 7.44 (1, d, J = 7.0 Hz), 7.18-7.34 (4, m), 2.57 (1, 1/2 AB, J = 12.8 Hz), 2.34 (1, 1/2 AB), 1.76 (3, br. s.), 1.01 (3, s), 0.89 (3, s); ^{13}C NMR d 146.80 (s), 145.93 (s), 140.32 (s), 140.08 (s), 128.63 (d), 128.38 (d), 127.13 (d), 126.80 (d), 126.55 (d), 125.90 (d), 119.60 (d), 119.45 (d), 105.29 (s), 98.21 (s), 52.18 (t), 46.09 (s), 30.47 (q), 28.14 (q), 26.45 (q); HRMS *m/z* calcd. for $C_{19}H_{20}O_2$ 280.1463, found 280.1461; Anal. calcd. C 81.40 H 7.19, found C 81.45 H 7.24. **Bifluorenol 6** (24) : ^{13}C NMR d 145.13 (s), 140.56 (s), 129.06 (d), 127.01 (d), 125.18 (d), 119.20 (d), 86.40 (s).

Preparation of hemiacetal 4a and alcohol 7. Table I, entry 2 : 5 mmol. (0.901 g) of **1a** and 5 mmol. (0.491 g) of **2a** were used to give products **7** (31%) and **4a** (16%) which were isolated by flash chromatography (ether-pentane : 10-90 and 20-80). **Alcohol 7** : mp 98-99°C (ether-pentane); IR (CCl_4) 3630, 3420 cm^{-1}; ^1H NMR (200 MHz) d 7.84-7.89 (1, m), 7.57-7.72 (3, m), 7.23-7.37 (4, m), 2.36 (1, 1/2 AB, J = 12.4 Hz), 2.32 (1, 1/2 AB), 1.92 (1, br. s.), 1.36 (3, s), 1.28 (3, s), 1.08 (3, s); ^{13}C NMR d 145.20 (s), 143.55 (s), 141.91 (s), 141.52 (s), 128.63 (d), 128.10 (d), 127.30 (d), 126.83 (d), 126.15 (d), 125.88 (d), 119.64 (d), 119.52 (d), 75.53 (s), 68.10 (s), 48.30 (t), 37.10 (s), 28.45 (q), 27.46 (q), 26.90 (q). HMRS *m/z* calcd. for $C_{19}H_{20}O$ 264.15141, found 264.1511; Anal. calcd. C 86.31 H 7.63, found C 86.36 H 7.64.

Reductive Cross Coupling of Fluorenone 1a and Methyl Vinyl Ketone 2b.

Preparation of 8 and 3b . Table I, entry 3 : 5 mmol. (0.901 g) of **1a** and 5 mmol. (0.350 g) of **2b** were used. Addition was done as in entry 1 to give compounds **8** (53%) and **3b** (32%) which were isolated by flash chromatography (ether-pentane : 30-70 and 50-50).

Table I, entry 4 : 5 mmol. (0.901 g) of **1a** and 5 mmol. (0.350 g) of **2b** were used with 15 mmol. of $TiCl_4$-Mg in 20 ml of THF. Addition of **1a** and **2b** was performed without a cooling bath, so that the temperature of the suspension warmed to 30-35 °C. Products **8** (8%) and **3b** (57%) were isolated by flash chromatography. **Ketol 8** : mp 194-195 °C (ether-pentane); IR ($CDCl_3$) 3420, 1710 cm^{-1}; ^1H NMR (200 MHz) d 7.00-7.46 (16, m), 3.10 (2, m), 2.43 (1, br. s), 1.75 (3, s), 1.56 (2, m); ^{13}C NMR d 208.98 (s), 146.90 (s) (2C), 145.81 (s) (2C), 141.87 (s) (2C), 140.28 (s) (2C), 128.82 (d) (2C), 127.57 (d) (2C), 126.63 (d) (2C), 126.49 (d) (2C), 125.11 (d) (2C), 124.82 (d) (2C), 119.09 (d) (4C), 86.77 (s), 60.73 (s), 38.78 (t), 29.93 (q), 26.29 (t). HRMS *m/z* calcd. for $C_{30}H_{24}O_2$ 416.17762, found 416.1770. **Ketol 3b** : IR (film) 3410, 1710 cm^{-1}; ^1H NMR (200 MHz) d 7.22-7.65 (8, m), 2.64 (1, br. s), 2.34 (2, m), 1.99 (2, m), 1.86 (3, s); ^{13}C NMR d 208.19 (s), 147.94 (s) (2C), 139.43 (s) (2C), 129.08 (d) (2C), 128.08 (d) (2C), 123.62 (d) (2C), 119.98 (d) (2C), 81.71 (s), 38.53 (t), 33.23 (t), 29.77 (q). HRMS *m/z* calcd. for $C_{17}H_{16}O_2$ 252.11502, found 252.1165.

Reductive Cross Coupling of Fluorenone 1a and (+)-Pulegone 2c.

Preparation of enol ether 5c. Table I, entry 5 : 5 mmol. (0.901 g) of **1a** and 5 mmol. (0.751 g) of **2c** were used to

yield 5c (63%) which was isolated by flash chromatography (ether-pentane : 5-95). **Enol ether 5c** : mp 108-109 °C (pentane); [α]$_{578}^{20}$ = +25° ($CHCl_3$, c 2.1); IR (CCl_4) 1720, 1290, 1210, 1175, 1110, 990, 930 cm^{-1}; ^1H NMR (250 MHz) d 6.46 (4, d, J = 8.5 Hz), 6.21 (2, m), 6.08 (2, m), 1.76-2.34 (6, m), 1.40 (1, m), 1.09 (3, d, J = 7.5 Hz), 0.90 (3, s), 0.85 (3, s); ^{13}C NMR d 149.81 (s), 145.84 (s), 145.50 (s), 140.60 (s), 140.43 (s), 128.83 (d)(2C), 126.88 (d)(2C), 125.89 (d), 125.72 (d), 119.69 (d)(2C), 115.79 (s), 98.54 (s), 48.85 (s), 31.60 (t), 31.34 (t), 29.74 (d), 24.43 (q), 23.94 (q), 21.39 (q), 19.76 (t); HRMS *m/z* calcd. for $C_{23}H_{24}O$ 316.1827, found 316.1834; Anal. calcd. C 87.30 H 7.64, found C 87.38 H 7.73.

Preparation of hemiacetals 4c and 4c', enol ether 5c and bifluorylidene 9. Table I, entry 6 : 3.3 mmol. (0.595 g) of 1a and 3.3 mmol. (0.502 g) of 2c were used. Addition of 1a and 2c was done as in entry 4 to give 5c (15%), 9 (10%), 4c (24%) and 4c' (34%) which were isolated by flash chromatography (ether-pentane : 5-95, 10-90 and 15-85). **Hemiacetal 4c** : mp 130-131 °C (ether-pentane); [α]$_{578}^{24}$ = -13° ($CHCl_3$, c 1); IR (CCl_4) 3610, 3430 cm^{-1}; ^1H NMR (200 MHz) d 7.16-7.68 (8, m), 1.97-2.10 (3, m), 1.50-1.70 (5, m), 1.17 (3, s), 1.03 (3, d, J = 6.1 Hz), 0.59 (3, s); HRMS *m/z* calcd. for $C_{23}H_{26}O_2$ 334.19327, found 334.1933; Anal. calcd. C 82.59 H 7.84, found C 82.59 H 7.84. **Hemiacetal 4c'** : mp 128-129 °C (ether-pentane); [α]$_{578}^{24}$ = +39° ($CHCl_3$, c 1); IR (CCl_4) 3600, 3410 cm^{-1}; ^1H NMR (200 MHz) d 7.99 (1, d, J = 7.1 Hz), 7.59 (2, m), 7.45 (1, d, J = 7.5 Hz), 7.18-7.37 (4, m), 2.83 (1, broad d, J = 8.2 Hz), 1.70-2.17 (5, m), 1.25-1.40 (2, m), 1.09 (3, s), 1.02 (3, d, J = 5.8 Hz), 0.42 (3, s); ^{13}C NMR d 148.94 (s), 144.82 (s), 140.71 (s), 139.61 (s), 128.61 (d), 128.11 (d), 126.86 (d), 126.70 (d), 126.36 (d), 126.03 (d), 119.44 (d), 119.37 (d), 106.15 (s), 97.26 (s), 49.28 (s), 48.72 (d), 48.65 (t), 31.72 (t), 28.57 (d), 24.32 (q), 23.93 (q), 22.05 (q), 21.63 (t); Anal. calcd. for $C_{23}H_{26}O_2$ C 82.59 H 7.84, found C 82.64 H 7.83.

Reductive Cross Coupling of Xanthone 1b and (+)-Pulegone 2c.

Preparation of enol ether 5d. Table I, entry 7: 5 mmol. (0.981 g) of 1b and 5 mmol. (0.751 g) of 2c were used to give 5d (45%) which was isolated by flash chromatography (pentane). **Enol ether 5d** : mp 105-106 °C; IR ($CDCl_3$) 3080, 1720, 1655, 1250, 910 cm^{-1}; ^1H NMR (200 MHz) d 7.49 (2, m), 7.19 (6, m), 2.44 (1, m), 1.73-2.06 (5, m), 1.17-1.43 (1, m), 1.10 (3, d, J = 6.0 Hz), 0.57 (3, s), 0.56 (3, s); ^{13}C NMR d 151.18 (s)(2C), 148.48 (s), 128.05 (d)(2C), 126.39 (d), 126.30 (d), 125.70 (s), 125.55 (s), 122.77 (d)(2C), 116.02 (d)(2C), 112.22 (s), 86.43 (s), 52.92 (s), 31.14 (t), 30.97 (t), 29.50 (d), 24.49 (q), 24.00 (q), 21.36 (q), 19.21 (t); HRMS *m/z* calcd. for $C_{23}H_{24}O_2$ 332.1776, found 332.1778; Anal. calcd. C 83.10 H 7.28, found C 83.13 H 7.21.

Preparation of hemiacetals 4d and 4d' and enol ether 5d. Table I, entry 8 : 3.3 mmol. (0.647 g) of 1b and 3.3 mmol. (0.502 g) of 2c were used. Addition was done as in entry 6 to give 5d (23%), 4d (12%) and 4d' (23%) which were isolated by flash chromatography (ether -pentane : 10-90 and 30-70). **Hemiacetal 4d** : IR (CCl_4): 3440, 1605, 1585 cm^{-1}. **Hemiacetal 4d'** : mp 155-156 °C (ether-pentane); [α]$_{578}^{24}$ = +59° ($CHCl_3$, c 1); IR (CCl_4) 3420, 1600, 1570 cm^{-1}; ^1H NMR (200 MHz) d 8.33 (1, m), 7.61 (1, m), 7.12-7.33 (6, m), 2.22-2.36 (2, m), 1.26-1.94 (6, m), 1.01 (3, d, J = 6.2 Hz), 0.61 (3, s), 0.46 (3, s); ^{13}C NMR d 151.69 (s), 151.61 (s), 128.27 (s), 128.02 (d), 127.95 (d), 127.85 (d), 126.78 (d), 125.82 (s), 123.40 (d), 122.49 (d), 116.25 (d), 115.64 (d), 106.26

(s), 86.01 (s), 51.45 (s), 48.02 (t), 47.13 (d), 31.63 (t), 29.04 (d), 24.14 (q), 23.40 (q), 22.14 (q), 21.26 (t); HRMS *m/z* calcd. for $C_{23}H_{26}O_3$ 350.18818, found 350.1886; Anal. calcd. C 78.83 H 7.48, found C 78.53 H 7.45.

Reductive Cross Coupling of Fluorenone 1a and (-)-Carvone 2d.

Preparation of 3d , 3d' and 10 : Table I, entry 9 : 5 mmol. (0.901 g) of **1a** and 5 mmol. (0.750 g) of **2d** were used to give **3d** (5%), a mixture of diastereoisomers **3d'** (60%) and **10** (10%) which were isolated by flash chromatography (ether-pentane : 15-85 and 30-70)

Ketol 3d : mp 236 °C ($CHCl_3$); $[\alpha]_{578}^{24}$ = +35.8 ($CHCl_3$, c 1); IR ($CDCl_3$) 3600, 3020, 1700, 1220, 1030, 1005, 905 cm^{-1}; ^1H NMR (200 MHz) d 7.59-7.65 (3, m), 7.25-7.44 (5, m), 4.97 (1, br. s), 4.75 (1, br. s), 2.68-2.79 (3, m), 2.48 (2, m), 2.25 (1, td, J = 13.1 Hz, J = 4.7 Hz), 1.86 (3, s), 0.32 (3, d, J= 7.3 Hz); ^{13}C NMR d 214.26 (s), 148.02 (s), 147.67 (s), 146.43 (s), 140.24 (s), 139.29 (s), 129.23 (d) (2C), 128.42 (d), 127.57 (d), 125.48 (d), 123.82 (d), 120.19 (d), 120.09 (d), 112.77 (t), 83.04 (s), 46.76 (d), 43.16 (d), 41.02 (t), 40.16 (d), 22.80 (t), 22.22 (q), 12.02 (q); HRMS *m/z* calcd. for $C_{23}H_{24}O_2$ 332.1776, found 332.1774; Anal. calcd. C 83.10 H 7.28, found C 82.40 H 7.30. **Ketols 3d'** (mixture of diastereoisomers): IR (CCl_4): 3550, 3420, 3040, 1720, 1645, 1260, 1020, 855 cm^{-1}; major one: ^1H NMR (200 MHz) d 7.58-7.62 (3, m), 7.24-7.44 (5, m), 4.84 (2, m), 2.61-2.75 (2, m), 2.33-2.39 (2, m), 2.00-2.27 (3, m), 1.85 (3, s), 0.22 (3, d, J = 7 Hz); ^{13}C NMR d 213.75 (s), 147.86 (s), 147.73 (s), 147.44 (s), 140.11 (s), 139.09 (s), 128.98 (d), 128.93 (d), 128.27 (d), 127.42 (d), 125.60 (d), 123.45 (d), 119.98 (d), 119.87 (d), 109.81 (t), 82.84 (s), 48.53 (d), 46.07 (d), 44.69 (d), 41.97 (t), 25.61 (t), 20.71 (q), 11.41 (q). **Triol 10** : mp 242 °C ($CHCl_3$); $[\alpha]_{578}^{20}$ = -7 ° ($CHCl_3$, c 2.3); IR ($CDCl_3$) 3600,3010, 1960, 1920, 1640, 1610, 1290, 1180, 1020, 1000, 890 cm^{-1}; ^1H NMR (250 MHz) d 7.00-7.75 (16, m), 4.89 (1, br. s), 4.85 (1, br. s), 3.23 (1, broad d, J = 12.9 Hz), 2.68 (1, m), 2.23-2.46 (3, m), 1.90 (3, s), 1.51 (1, m), 0.96 (1, m), -0.84 (3, d, J = 7.0 Hz); ^{13}C NMR d 150.50 (s), 148.40 (s), 148.24 (s), 147.49 (s), 146.24 (s), 140.89 (s), 140.10 (s), 139.54 (s), 138.87 (s), 128.79 (d), 128.71 (d), 128.47 (d), 128.35 (d), 127.77 (d), 127.48 (d), 127.25 (d), 127.19 (d), 126.27 (d), 125.41 (d)(2C), 123,81 (d), 119.77 (d)(2C), 119.67 (d), 119.51 (d), 108.79 (t), 86.00 (s), 83.93 (s), 80.24 (s), 44.88 (d), 40.60 (d), 36.34 (d), 32.99 (t), 26.02 (t), 21.64 (q), 8.69 (q) ; HRMS *m/z* calcd. for $C_{23}H_{25}O_2$ 333.1854, found 333.1852; Anal. calcd. for $C_{36}H_{34}O_3$ C 84.02 H 6.66, found C 84.10 H 6.77.

Reductive Cross Coupling of Fluorenone 1a and Isophorone 2e.

Preparation of 11. Table I, entry 10 : 5 mmol. (0.901 g) of **1a** and 5 mmol. (0.691 g) of **2e** were used with 20 mmol. of $TiCl_4$-Mg in 20 ml of THF. Addition to the complex was performed as in entry 1 to give **11** (40%) which was isolated by flash chromatography along with unchanged **1a** (233 mg; 26%). **Hydrocarbon 11** : mp 257 °C (hexane-ether); IR (CCl_4) 3050, 1440, 1425 cm^{-1}; ^1H NMR (200 MHz) d 7.98 (1, m), 7.89 (1, m), 7.77 (2,m), 7.30 (4, m), 7.18 (1, br. s), 2.86 (2, s), 2.08 (2, br. s), 1.97 (3, br. s), 1.04 (6, s); ^{13}C NMR d 143.72 (s), 141.62 (s), 139.67 (s), 139.38 (s), 138.59 (s), 130.74 (s), 125.84 (s), 126.50 (d), 126.45 (d), 126.14 (d), 126.07 (d), 125.31 (d), 125.25 (d), 123.15 (d), 119.41 (d), 44.74 (t), 42.93 (t), 31.81 (s), 28.96 (q)(2C), 24.86 (q); HRMS *m/z* calcd. for $C_{22}H_{22}$ 286.1721, found 286.1715.

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