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Photoreactivity of α-Tetrasubstituted Arylketones: Production and Asymmetric Tautomerization of Arylenols

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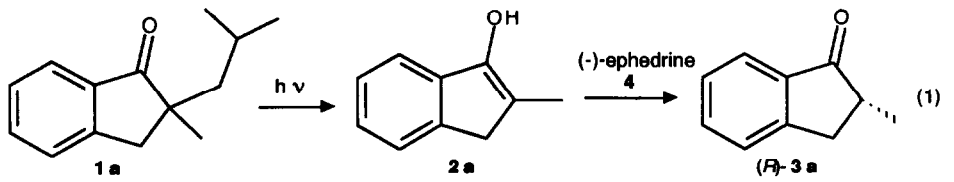
Abstract: In the presence of catalytic amounts of optically active aminoalcohols, the irradiation of α-disubstituted indanones, tetralones and propiophenones bearing at least one hydrogen in the γ-position led to Norrish type II cleavage compounds which were obtained with enantiomeric excesses reaching 89 %. The influence of the reaction conditions (temperature, wavelength of the UV light and nature of the aminoalcohol) has been analyzed.

INTRODUCTION

Intensive research work has been devoted to the synthesis and reactivity of enols[1] and to the asymmetric protonation of enolates[2] whereas to date the asymmetric protonation of a simple enol function has not been extensively explored.[3-5] In addition, photochemical approaches to asymmetric syntheses in general are relatively scarce.[6]

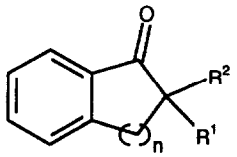
During the past few years, we have been largely concerned with the asymmetric protonation of dienols produced by a Norrish-type II photorearrangement of α,β-unsaturated carbonyl compounds.[7-9] The mechanistic model that we have proposed to rationalize the geometric constraints responsible for the enantioselective discrimination step, involves principally the enol part of the dienol[9] and could apply equally well to protonation of simple prochiral enols. As simple enols could be generated from a Norrish-type II photoelimination,[10] we have examined the behaviour of 2-methyl-2-isobutylindan-1-one **1a** under irradiation at room temperature with a nitrogen laser (λ = 337 nm). Thus, we have disclosed the formation of the prochiral enol **2a** which was stable in pure acetonitrile solutions but tautomerized selectively to (*R*)-**3a** in the presence of (-)-ephedrine **4** (Eq.1).[4]

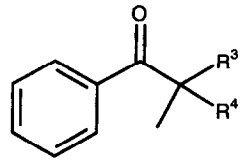


In this work we have tried to determine the scope and limitations of the previous observations, made with **1a**[4], with various phenylketones and to examine the conditions which might best favour the enantioselective tautomerization of the photoenols.

For these reasons, we have examined the effects of varying the solvent, the temperature, the wavelength

and the optically active aminoalcohols on the reaction, using **1a** as substrate. In order to evaluate the effects of strain and steric hindrance on the protonation of the photoenol, we studied the photoreactivity of **1b** and **1c**.[11] The photoreactivity of **5a** and **5b** leading to an acyclic enol was also examined. The highly efficient deracemization of benzoïn in the ground state[2d,3] would involve an enediol. With this purpose we also prepared and irradiated **1d**.





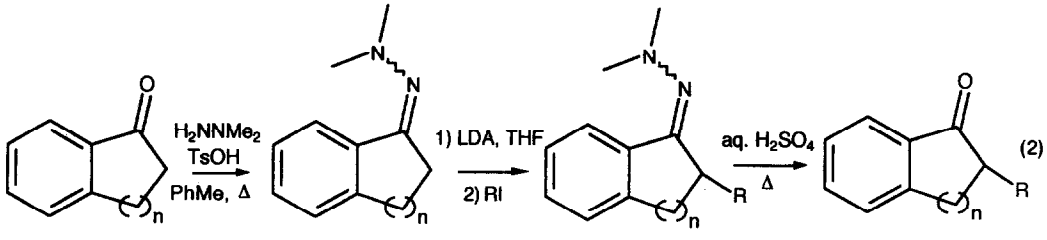
1a n = 1, R^1 = Me, R^2 = *i*-Bu
1b n = 2, R^1 = Me, R^2 = *i*-Bu
1c n = 2, R^1 = CH_2Ph, R^2 = *i*-Bu
1d n = 1, R^1 = OH, R^2 = *i*-Bu

3a n = 1, R^1 = Me, R^2 = H
3b n = 2, R^1 = Me, R^2 = H
3c n = 2, R^1 = CH_2Ph, R^2 = H
3d n = 1, R^1 = OH, R^2 = H

5a R^3 = R^4 = *n*-Pr
5b R^3 = R^4 = *i*-Bu

PREPARATION OF THE STARTING KETONES

As the direct alkylation of indan- and tetral-1-one led to low yields of the monosubstituted compounds, the synthesis of the required ketones was carried out *via* hydrazones **7**. The first alkylation was achieved using lithium disopropyl amide as base (Eq. 2). The second alkylation was made on the regenerated ketone under phase transfer conditions (P.T.C.)[12] or by employing sodium hexamethyldisilazane[13] (Eq. 3 and 4). As the hydrogenation of the double bond of **1e** or **1f** over PtO_2 afforded high yields of **1a** and **1b** respectively, the alkylation of **3a** and **3b** using 2-methylpropenyl chloride offered another efficient way to prepare these starting materials.

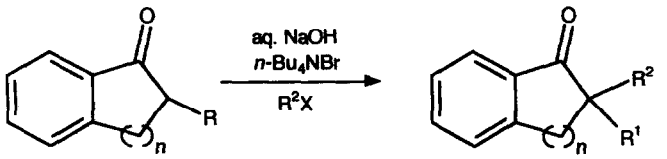


6a n = 1
6b n = 2

7a n = 1 (98%)
7b n = 2 (97%)

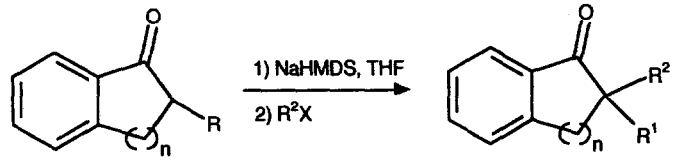
8a n = 1, R = Me (90%)
8b n = 2, R = Me (84%)
8c n = 1, R = *i*-Bu (81%)
8d n = 2, R = *i*-Bu (86%)

3a n = 1, R = Me (84%)
3b n = 2, R = Me (84%)
3e n = 1, R = *i*-Bu (92%)
3f n = 2, R = *i*-Bu (96%)



3a n = 1, R = Me
3b n = 2, R = Me
3e n = 1, R = *i*-Bu

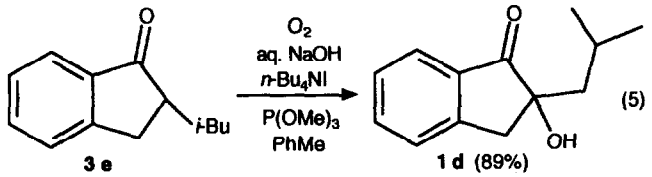
1a n = 1, R^1 = Me, R^2 = *i*-Bu (X = I, 34)
1e n = 1, R^1 = Me, R^2 = $CH_2C(Me)=CH_2$ (X = Cl, 83%)
1f n = 2, R^1 = Me, R^2 = $CH_2C(Me)=CH_2$ (X =Cl, 57%)



3b n = 2, R = Me
3f n = 2, R = *i*-Bu

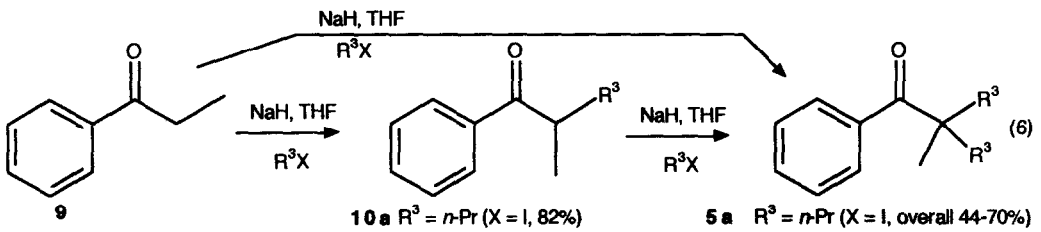
1c n = 2, R^1 = CH_2Ph, R^2 = *i*-Bu (X = Br, 95%)
1f n = 2, R^1 = Me, R^2 = $CH_2C(Me)=CH_2$ (X = Cl, 57%)

The α-ketol **1d** was obtained from **3e** by oxidation with oxygen under P.T.C. in the presence of trimethylphosphite as the reductive species[14] (Eq.5).



3e **1d** (89%)

The alkylation of propiophenone was carried out sequentially to give **10** then **5** (overall yields: 44% for **5a**, 9% for **5b**) or preferentially in one step (overall yields: 70% for **5a**, 33% for **5b**) (Eq. 6).



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10a R^3 = *n*-Pr (X = I, 82%)
10b R^3 = *i*-Bu (X = Br, 46%)

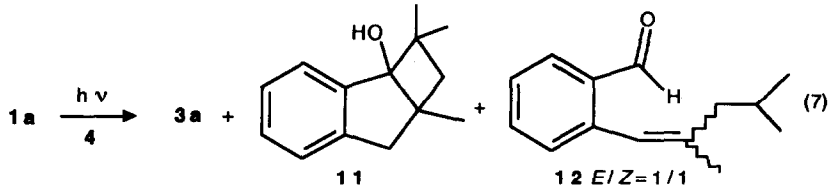
5a R^3 = *n*-Pr (X = I, overall 44-70%)
5b R^3 = *i*-Bu (X = Br, overall 9-33%)

IRRADIATION RESULTS

1) 2-Methyl-2-isobutylindan-1-one.

a) (-)-Ephedrine (4) as chiral protic species. The irradiation of a deoxygenated acetonitrile solution of **1a** and **4** (0.1 equiv.) carried out at -3°C with a medium pressure lamp filtered by pyrex induced 84% conversion of the starting ketone leading to **3a** (50 %), **11** (2 %) and **12** (12 %) (Eq. 7). No optical activity was observed for **11** while **3a** was formed with a 37 % enantiomeric excess (e. e.) and the *R* configuration was

attributed to the major enantiomer from $[\alpha]_D$ comparison with literature data.[15]



Unfortunately, unreproducible e. e.'s were obtained when irradiations were carried out at temperatures inferior to 5°C. As the intermediate enol **2a** displays high stability at room temperature in acetonitrile in the absence of protic species,[4] we envisaged that its rate of tautomerisation by **4** slowed down with the temperature and that an undefined percentage of the tautomerization might occur during the workup. Thus, solutions of **1a** and **4** were irradiated for 1.25 h at 0, - 27 or - 40°C and kept in the dark at these temperatures for various periods before being analyzed. From the results listed in Table 1, it appears that the e.e. depend not only on the nature of the solvent but also on the waiting period in the dark. In acetonitrile differences of e.e. up to 10% could be observed at -40 or 0°C, depending on the waiting period while a smaller effect has been detected in hexane solutions at -27°C. These observations suggest that the rate of the tautomerization of **2a** is higher in hexane than in acetonitrile and confirm that the enol can accumulate in a polar solvent even in the presence of protic species. We will return to this point in the discussion.

Table 1: Exemplification of the low rate of tautomerization of **2a** by **4**.

Solvent	t°C	Waiting period h	Conversion %	**3a** Selectivity %[a]	e. e. %
MeCN	- 40	0	90	74	43
MeCN	- 40	15	90	82	52
MeCN	- 40	24	90	82	53
MeCN	- 40	40	90	78	51
MeCN	0	0	b	b	34
MeCN	0	15	b	b	43
hexane	- 27	0	94	50	39
hexane	- 27	10	97	45	41

[a] Selectivity is the yield in isolated **3a** calculated on the amount of unrecovered **1a**.

[b] Not determined.

As there were no great differences in e. e.'s but better selectivities in using acetonitrile rather than hexane as the solvent (Table 1), acetonitrile was mainly used in the following reactions. Based on the preceeding observations, it was also decided to maintain the photolyzed solutions at the irradiation temperature for at least 15 h before carrying out the workup. Thus, reproducible results were obtained between + 60 and - 38°C (Table 2). In addition, we observed that the irradiation time did not greatly influence the e. e., even if the selectivity was slightly reduced for longer irradiation times (Table 3). At low temperatures, small amounts of **12** (7-12 %) were also obtained.

At room temperature and while using a high pressure lamp filtered with a Wood glass ($\lambda = 366$ nm) instead of a medium pressure lamp filtered by pyrex, **3a** was obtained with higher e. e. and selectivity (Table 4). Furthermore acetonitrile seems to remain the solvent of choice for our purpose and we note that the presence of

small amounts of water did not lower the e. e..

Table 2: Influence of the reaction temperature on the enantioselectivity of **3a**.[a]

t°C	+ 60	+ 51	+ 39	+ 20	+ 13	+ 10	+ 5	0	- 8	- 19	- 30	- 38
Conversion %	94	97	92	87	97	89	98	92	95	92	89	94
3a Yield %	64	67	59	65	64	67	84	64	80	70	74	67
3a e. e. %	25	23	12	10	35	35	36	41	43	45	47	49

[a] Acetonitrile solutions of **1a** ($c \approx 4 \times 10^{-3}$ M) irradiated for 75 mn at $\lambda > 290$ nm in the presence of **4** ($c \approx 4 \times 10^{-4}$ M) and then kept in the dark at the same temperature for 15-20 h.

Table 3: Influence of the irradiation time on the selectivity in **3a**.[a]

Irradiation time h	0.25	0.5	0.75	1.25	2	3	4
Conversion %	60	88	92	94	94	96	98
3a Selectivity %	82	77	84	71	68	66	68
3a e. e. %	51	49	51	51	51	46	47

[a] Acetonitrile solutions of **1a** ($c \approx 4 \times 10^{-3}$ M) irradiated at - 38°C and $\lambda > 290$ nm in the presence of **4** ($c \approx 4 \times 10^{-4}$ M) and then kept in the dark at - 38°C for 15-20 h.

Table 4: Influence of the solvent on the enantioselectivity.[a]

Solvent	Conversion %	**3a**		
		Selectivity %	e. e. %	Conf.
MeCN	70	91	45	*R*
PhMe	51	73	24	*R*
$CHCl_3$	43	72	24	*R*
CH_2Cl_2	75	88	22	*R*
MeCN[b]	77	83	43	*R*

[a] Solutions of **1a** ($c \approx 4 \times 10^{-3}$ M) irradiated at room temperature, $\lambda = 366$ nm and for 1.25 h in the presence of **4** ($c \approx 4 \times 10^{-4}$ M).

[b] Irradiation in the presence of water (7 equiv.) for 2 h.

The modification of the e.e. with the nature of the UV light and the slight decrease in the e. e. of isolated **3a** when its precursor is subjected to photolysis for long periods (Table 3) might be due to a photoracemisation of **3a** which could increase at shorter wavelengths.

Therefore, acetonitrile solutions of optically active **3a** were irradiated at different wavelengths (Table 5). The racemisation was indeed observed and furthermore, a *Z/E* mixture of the cleavage product **13** was isolated (Eq. 8).

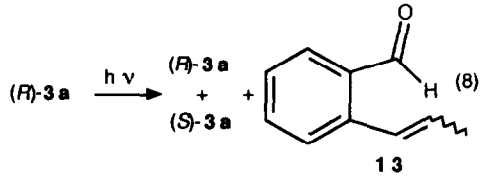


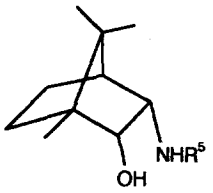
Table 5: Photoracemisation of **3a** in acetonitrile solutions ($c \approx 10^{-2}$ M) irradiated at room temperature for 2 h.

e. e. % of starting **3a**	λ nm	Recovered **3a**		**13**
		Yield %	e. e. %	Yield %
26	> 290	84	10	8
50	366	83	38	7

b) Other optically active protic species. It was precedently shown that i) the enantioselective tautomerization of dienols derived from esters required a chiral aminoalcohol as protic catalyst to be efficient, and ii) the resulting e. e. was very sensitive to the structure and substitution of the aminoalcohol.[7] Irradiations of **1a** led to similar observations: no or very low e. e.'s when using (*S*)-α-methyl benzylamine, (*S*)-octan-2-ol or (-)-

mandelic acid while the aminoalcohols **14** to **18** afforded **3a** with 24-36 % e. e. (Table 6).

14 Norephedrine
15 (+)-cinchonine
16 (-)-cinchonidine



17 $R^5 = H$
18 $R^5 = i\text{-Pr}$
19 $R^5 = Me$
20 $R^5 = CH_2Ph$

Table 6: Use of aminoalcohols **14-18** for the tautomerization of **2a**.[a]

Aminoalcohol	Conversion	3a		
	%	Yield %	e. e. %	Conf.
14	90	68	24	*R*
15	90	70	27	*R*
16	92	67	26	*S*
17	b	65	36	*R*
18	b	b	26	*R*

[a] Acetonitrile solutions of **1a** ($c \approx 4 \times 10^{-3}$ M) irradiated at - 40°C and $\lambda > 290$ nm for 2 h in the presence of **14** to **18** ($c \approx 4 \times 10^{-4}$ M) and then kept in the dark between -40 and -10°C for 15 h. [b] Not determined.

2) 2-Methyl-2-isobutyl-(3,4)-dihydronaphthalen-1-one.

Preliminary experiments carried out with **1b** in MeCN and followed by circular dichroism showed that the enol **2b** was much more stable than **2a** in the presence of protic species. For example, **2a** was fully tautomerized to **3a** in less than 1 minute by adding 0.1 equiv. of **4** at room temperature while the complete transformation of **2b** to **3b** required 2.5 h under similar conditions. Therefore, irradiations of **1b** at -40°C were followed by a waiting period of 3 days at -40°C in the dark before proceeding to the workup. For reactions realized at room temperature, the workup was carried out after 20 h in the dark. From results reported in Table 7, it appears that the irradiations at 366 nm and a low temperature gave better results. Furthermore, we were delighted to observe e. e. as high as 89 % in using the aminobornanol derivative **18**.

Table 7: Influence of the experimental conditions on the formation of **3b**.[a]

Aminoalcohol	λ	Irradiation		Conversion	3b		
	nm	t°C	time h	%	Yield %	e. e. %[b]	Conf.[b]
4	> 290	- 40	1.5	98	69	42	*R*
4	366	RT	0.75	69	60	41	*R*
4	366	- 40	1	64	52	54	*R*
17	366	RT	0.75	86	66	63	*R*
17	366	- 40	1	73	57	71	*R*
18	366	- 40	1	60	40	89[c]	*R*
19	366	- 40	1	79	56	76	*R*
20	366	- 40	1	d	47	83	*R*

[a] Acetonitrile solutions of **1b** ($c \approx 4 \times 10^{-3}$ M) irradiated in the presence of aminoalcohols ($c \approx 4$ to 5×10^{-4} M) and then kept in the dark (see text). [b] Determined from $[\alpha]_D$ comparison with literature data.[15] [c] Also determined from ^1H NMR in the presence of Eu(hfc)$_3$. [d] Not determined.

3) 2-Benzyl-2-isobutyl-(3,4)-dihydronaphthalen-1-one.

Based on the results obtained from **1a** and **1b**, the irradiation of **1c** was carried out in MeCN in the presence

of 0.1 equiv. of **17**, **18** or **20** (Table 8). The best e. e. was obtained with the latter aminoalcohol.

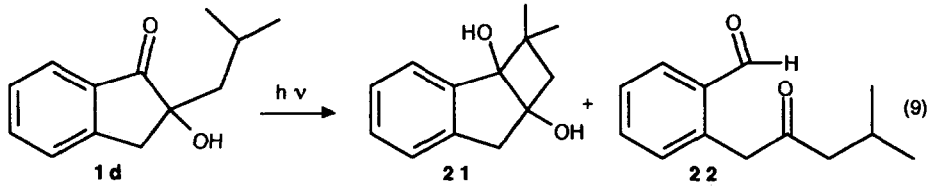
Table 8: Influence of the nature of the aminoalcohol on the e. e. of **3c**.[a]

Aminoalcohol	3c		
	Yield %	e. e. %[b]	Conf.[b]
17	50	18	*S*
18	55	23	*S*
20	49	47	*S*

[a] Acetonitrile solutions of **1c** ($c \approx 4 \times 10^{-3}$ M) irradiated at - 40°C and $\lambda > 290$ nm for 1.5 h in the presence of **17**, **18** or **20** ($c \approx 4 \times 10^{-4}$ M) and then kept in the dark for 3 days at -40°C. [b] Determined from $[\alpha]_D$ comparison with literature data.[16]

4) 2-Hydroxy-2-isobutylindan-1-one.

Irradiation of acetonitrile solutions of **1d** in the presence or absence of **4** at $\lambda > 290$ nm did not afford **3d** but led to diol **21** and ketoaldehyde **22** (Eq.9 and Table 9), therefore the study of the reactivity of this particular ketol was shortened.



1d **21** **22**

Table 9: Irradiation of acetonitrile solutions of **1d** ($c \approx 4 \times 10^{-3}$ M) at $\lambda > 290$ nm.

4 equiv.	Irradiation t°C	Irradiation time h	Conversion %	**21** Yield %	**22** Yield %
0.1	- 40	2	19	6	6
0.1	- 40	8	59	a	14
0	RT	8	70	34	34

[a] Not determined

5) Linear arylketones: 1-phenyl-2-methyl-2-propylpentan-1-one and 1-phenyl-2-isobutyl-2,4-dimethylpentan-1-one.

The linear ketones **5a** and **5b** irradiated at $\lambda > 290$ nm and -40°C in the presence of (+)-ephedrine (0.1 equiv.) led to the expected ketones **10a** and **10b** but with too low yields or e. e.'s (Table 10) to envisage developing their study.

Table 10: Irradiation of acetonitrile solutions of **5a** and **5b** ($c \approx 4 \times 10^{-3}$ M).

Ketone	Solvent	Irradiation time h	Conversion %	**10** Yield %	e. e. %
5a	Hexane	0.5	68	**10a**, 5	a
5a	CH_2Cl_2	0.5	48	**10a**, 13	a
5a	MeCN	0.5	87	**10a**, 17	a
5a	Et_2O	0.5	81	**10a**, 5	a
5b	Hexane	1	93	**10b**, 47	9[b]

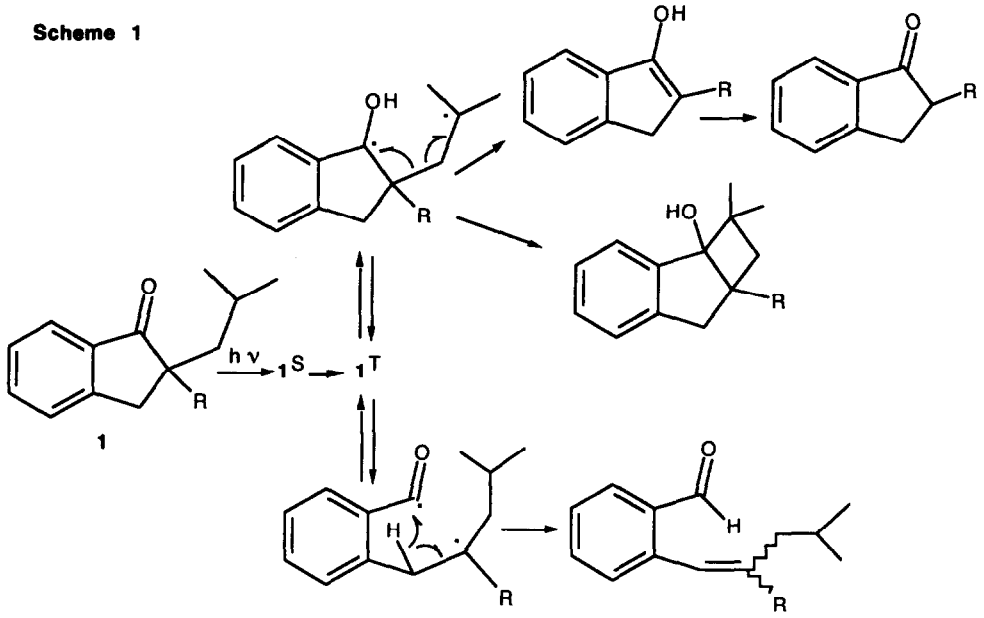
[a] Not determined. [b] Determined from ^{1}H NMR in the presence of Eu(hfc)$_3$.

DISCUSSION

The ketones **3a-3c**, **10a**, **10b** and cyclobutanols **11**, **21** are usual Norrish type II photoproducts,[10] while the aldehydes **12**, **13** and **22** are formed by the well known Norrish type I cleavage[17] (scheme 1). The complete quenching of the photoreactivity of **1a** by phenanthrene[18] indicates that these reactions pass via an excited triplet state as shown precedently for aromatic ketones.[10b,19] Although α-alkyl substitution usually enhances α-cleavage,[20] and cyclobutanol formation,[21] it is interesting to point out that the Norrish type II photoelimination remains the main observable process for **1a**, **1b**, **1c** and **5b**. No photoelimination is detected from **1d**; cyclobutanol formation and α-cleavage remain here competitive pathways although the benzoin structure generally favours an efficient α-cleavage producing radical species which induce free radical polymerisation.[22]

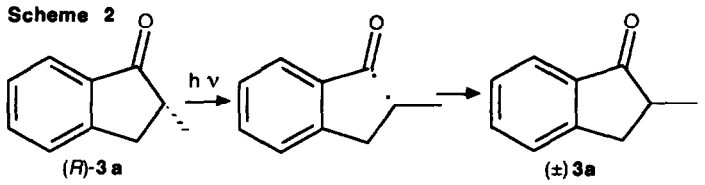
These remarks do not exclude the possibility that part of the photon energy could be lost by unproductive reactions from excited states of the substrates. Furthermore, the formation of biradicals from Norrish reactions is reversible.[20c] Since the main objective of the present work was the study of the asymmetric protonation of enols, we did not measure the quantum yields.

Scheme 1



The photoracemization of (*R*)-**3a** is easily explained by a Norrish type I affording a biradical which cyclizes to give a 1/1 mixture of the two enantiomers[20c,23] (Scheme 2).

Scheme 2



This photoracemization seems to be less important when using the longer wavelength (table 5). This observation can be explained by examination of the absorption coefficients in acetonitrile at 313 and 366 nm

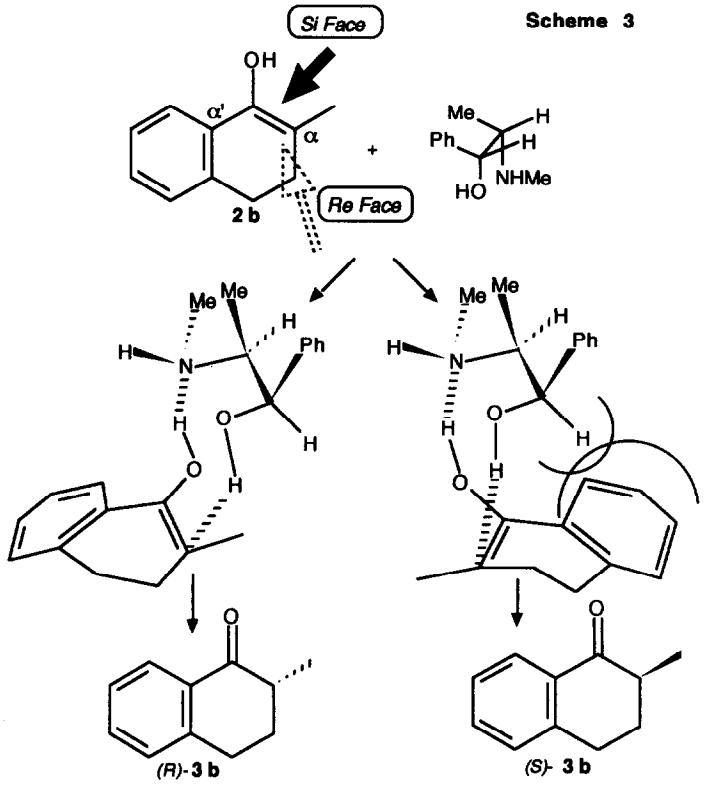
(wavelengths which correspond to the main emission of the lamps with the filters used) of the starting material (**1a**) and the photoproduct (**3a**) giving for **1a**: 76 and 4, and for **3a**: 63 and 2 respectively. The differences of the ε ratios $(\varepsilon_{1a}/\varepsilon_{3a})_{313}$= 1.2 and $(\varepsilon_{1a}/\varepsilon_{3a})_{366}$= 2 indicate that the photoracemization of **3a** can start at a lower concentration of this ketone, when a medium pressure mercury lamp is used.

The apparent less important racemization of **3a** observed when **1a** was irradiated at low temperatures, is assigned to the slower tautomerization of the enol **2a** under these conditions. Thus the concentration of **2a** gradually increases in the medium and the appearance of **3a** as its photocleavage product is minimized.

Concerning the enantioselective tautomerization step, we recall here to our preceeding reports concerning photodienols.[9] A 9-membered ring intermediate was thus suggested. Scheme 3 represents the two approaches of the dienol **2b** by (-)-ephedrine. Less steric constraints from the *Si* face than the *Re* face privilege the formation of the (*R*)-isomer. This model however does not rationalize the influence of the substituent of the amino group on the e. e. of **3**.

We need also to comment on the comparison of the tautomerization of enols and dienols. The asymmetric deconjugation of an α,β-unsaturated ester involves the intermediate formation of a *Z*-dienol. In contrast, the irradiation of **1b** led to the *E*-enol **2b**. Nevertheless, the preferred approach of (-)-ephedrine to both *Z*-dienol and *E*-enol is on the *Si* face leading in each case to the (*R*)-enantiomer. Besides, the unfavored approach seems to be due to interactions either with the acyl chain (mainly the β-substituent) in the case of the *Z*-dienol,[9] or with the aromatic group located in the α'-position in the case of **2b**. Further work would be required before being able to rationalize these unexpected observations.

Scheme 3



EXPERIMENTAL

General indications. Solvents were distilled under an argon atmosphere before use, THF and diethyl ether over Na/benzophenone, toluene and hexane over CaH_2 and acetonitrile over P_2O_5 and CaH_2 successively. Literature methods were used to prepare **17**[24] and its derivatives **18**,[25] **19** and **20**.[26] NMR spectra were recorded in $CDCl_3$ on CW 80-, AC 250-, AC 300-Bruker or Jeol (400 MHz) spectrometers. IR spectra were

recorded on a SP3-300-Philips spectrometer and UV spectra on an UV 5240-Beckman spectrometer. Optical rotations were measured on a 241-Perkin-Elmer polarimeter. Melting points were determined using either a Kofler or a Büchi apparatus. Mass spectra were recorded on a D 300-JEOL apparatus at the U.F.R of Pharmacy of this University. Elemental analysis were performed on a CHN 2400 Perkin Elmer machine. Merck silica gels (60 $PF_{254+366}$ or 60 40-63 μm) were used for chromatography.

Preparation of the starting ketones

Hydrazone synthesis. A toluene solution of ketone (**6a** or **6b**) containing 1,1-dimethylhydrazone (3 equiv.) and *p*-toluenesulfonic acid (0.1 equiv.) was heated under reflux for 16 h, the water formed was removed with a Dean Stark trap. After evaporation of the solvents, flash-chromatography of the residue eluting with AcOEt/petroleum ether (15/85) led to the hydrazone.

- indan-1-one N,N-dimethylhydrazone **7a:** Yield: 98 %. ^1H NMR (80 MHz): 2.8 (6 H, s), 3.0 (4 H, m), 7.3 (3 H, m), 8.8 (1 H, m). ^{13}C NMR (63 MHz): 28.7, 47, 121.9, 125.3, 126.8, 130.4, 138.7, 148.2, 168.6. IR (CCl_4): 2960, 2860, 1740, 1630.

- (3,4)-dihydro-(2 H)-naphthalen-1-one N,N-dimethylhydrazone **7b:** Yield: 97%. ^1H NMR (300 MHz): 1.8 (2 H, tt, J= 6. 6), 2.5 (6 H, s), 2.70 (2 H, t, J= 6), 2.74 (2 H, t, J= 6), 6.95-7.17 (3 H), 8.06 (1 H, dd, J= 6.8, 1). ^{13}C NMR (63 MHz): 22.5, 27.2, 29.5, 47.2, 124.9, 126, 128.5, 129.2, 132.9, 139.5, 160.9. IR (CCl_4): 2960, 2860, 2810, 1740. MS, m/e (%): 89 (15), 126 (22), 144 (14), 173 (17), 188 (100).

Monoalkylation of hydrazones. A THF solution of the hydrazone was added dropwise to a THF/hexane solution of LDA (1.15 equiv.) cooled to -40°C. After stirring for 3 h the alkyl iodide (1.07 equiv.) was added. Stirring was maintained for 18h and the mixture was allowed to reach room temperature. Usual workup was followed by flash-chromatography of the residue eluting with AcOEt/petroleum ether (10/90).

- 2-methyl-indan-1-one N,N-dimethylhydrazone **8a.** Yield: 90 %. ^1H NMR (80 MHz): 1.3 (3 H, d, J= 8), 2.55 (1 H, m), 2.5 (6 H, s), 3.0-3.6 (2 H), 7.3 (2 H, m), 7.8 (1 H, m), 8.5 (1 H, m). IR ($CHCl_3$): 2960, 2860, 1700, 1600, 1460.

- 2-methyl-(3,4)-dihydronaphthalen-1-one N,N-dimethylhydrazone **8b**. Yield: 84 %. ^1H NMR (80 MHz): 1.1 (3 H, d, J= 7), 1.5-2.30 (2 H), 2.5 (6 H, s), 2.7-3.05 (2 H), 3.7 (1 H, m), 7.2 (3 H, m), 8.1 (1 H, m). IR ($CHCl_3$): 2960, 2860, 1730, 1610, 1460, 1450.

- 2-isobutylindan-1-one N,N-dimethylhydrazone **8c.** Yield: 81 %. ^1H NMR (80 MHz, CCl_4): 0.91 (3 H, d, J= 6), 0.97 (3 H, d, J= 6), 1.1-2.1 (3 H, m), 2.5 (6 H, s), 2.6-3.4 (3 H, m), 7.2 (2 H, m), 7.7 (1 H, m), 8.4 (1 H, m). IR ($CHCl_3$): 2960, 2860, 1700, 1600, 1460.

- 2-isobutyl-(3,4)-dihydronaphthalen-1-one N,N-dimethylhydrazone **8d:** Yield: 86 %. ^1H NMR (80 MHz): 0.87 (3 H, d, J= 6), 0.96 (3 H, d, J= 6), 1.1- 2.0 (5 H, m), 2.5 (6 H, s), 2.7- 3.0 (2 H, m), 3.71 (1 H, m), 7.16 (1 H, m), 8 (1 H, m). IR ($CHCl_3$): 2950, 2860, 1725, 1600, 1460, 1450.

Deprotection of hydrazones. A mixture of the hydrazone (3 g) and aqueous 10% sulfuric acid(10 ml) was refluxed for 18 h. After cooling to room temperature, extraction with ether, neutralisation using aq. $NaHCO_3$, drying over $MgSO_4$ and evaporation of solvent, flash-chromatography of the residue eluting with AcOEt/petroleum ether (3/97) led to the ketone.

- 2-methylindan-1-one **3a**. Yield: 84 %. ^1H NMR (300 MHz): 1.3 (3 H, d, J= 7.3), 2.60-2.76 (2 H), 3.38 (1 H, dd, J= 17.8, 8.6), 7.35 (1 H, t, J= 7.5), 7.43 (1 H, d, J= 7.5), 7.56 (1 H, t, J= 7.5), 7.73 (1 H, d, J= 7.5). ^{13}C NMR (75 MHz): 16, 34.7, 41.8, 123.7, 126.4, 127.1, 134.5, 136.1, 153.2, 209.1. IR ($CHCl_3$):

3000, 2960, 2920, 2860, 2840, 1700, 1600, 1465, 1436, 1370, 1325, 1290. UV (MeCN): λ_{max}= 222 nm, ε= 600, λ_{max}= 298 nm, ε= 230, λ_{max}= 322 nm, ε= 45.

- 2-methyl-(3,4)-dihydronaphthalen-1-one **3b**. Yield: 84 %. ^{1}H NMR (300 MHz): 1.25 (3 H, d, J= 6.7), 1.86 (1 H, m), 2.17 (1 H, ddd, J= 13.2, 8.8, 4.4), 2.55 (1 H, m), 3 (2 H, m), 7.25 (2 H, m), 7.45 (1 H, dt, J= 7.2, 1), 8.03 (1 H, dd, J= 7.2, 1). ^{13}C NMR (75 MHz): 15.3, 28.7, 31.2, 42.5, 126.4, 127.2, 128.6, 132.2, 132.9, 144, 200.5. IR ($CHCl_3$): 2930, 1675, 1600, 1450. UV (MeCN) : λ_{max}= 222 nm, ε= 610, λ_{max}= 300 nm, ε= 280, λ_{max}= 315 nm, ε= 52.

-2-isobutylindan-1-one **3e**. Yield: 92 %. ^{1}H NMR (250 MHz): 1.0 (6 H, d, J= 6), 1.3 (1 H, m), 1.84 (2 H, m), 2.60- 2.76 (1 H), 2.80 (1 H, dd, J= 17, 4), 3,35 (1 H, dd, J= 17, 7.5), 7.2-7.8 (4 H). ^{13}C NMR (63 MHz): 21.6, 23.4, 26.5, 33.3, 40.5, 45.8, 123.8, 126.4, 127.2, 134.5, 136.6, 153.6, 209.3. IR (CCl_4): 2960, 1705, 1600, 1460. UV (MeCN): λ_{max}= 222 nm, ε= 860, λ_{max}= 298 nm, ε= 300, λ_{max}= 322 nm, ε= 74.

- 2-isobutyl-(3,4)-dihydronaphthalen-1-one **3f**. Yield: 96 %. ^{1}H NMR (300 MHz): 0.92 (3 H, d, J= 5.5), 0.96 (3 H, d, J= 6.7), 1.32 (1 H, ddd, J= 13.5, 8, 5.4), 1.7-1.9 (3 H), 2.24 (1 H, ddd, J= 13.5, 11.2, 4.5), 2.54 (1 H, m), 2.98 (2 H, q, J= 4.9), 7.22 (1 H, d, J= 9), 7.3 (1 H, dt, J= 9, 2), 7.45 (1 H, dt, J= 9, 2), 8.03 (1 H, dd, J= 9, 2). ^{13}C NMR (75 MHz): 21.7, 23.3, 25.3, 28, 28.3, 38.3, 45.3, 126.4, 127.4, 128.6, 132.5, 133, 143.8, 200.7. IR ($CHCl_3$): 2930, 2860, 1670, 1600, 1450. MS, m/e (%): 77 (13), 90 (49), 115 (28), 118 (20), 131 (32), 146 (100), 203 (15, M+1). UV (MeCN): λ_{max}= 220 nm, ε= 794, λ_{max}= 298 nm, ε= 316, λ_{max}= 325 nm, ε= 63.

Procedure for alkylation of **3a**, **3b** *and* **3e** *under P.T.C.* A mixture of aq. 50% sodium hydroxide (3 ml/mmol), ketone, alkylating reagent (6-7 equiv.), triethylbenzylammonium bromide (in the case of **3a**: 0.7 equiv., **3b**: 0.3 equiv., **3e**: 1.2 equiv.), sodium iodide (only in the case of **3a**: 2 equiv.) in methylene chloride or toluene (15 ml/mmol) was vigorously stirred for 3 to 11 days. Usual workup followed by flash-chromatography of the residue eluting with AcOEt/petroleum ether (3/97) afforded **1a**, **1e** or **1f**.

Procedure for alkylation of **3b** *and* **3f** *in using NaHMDS.* A THF solution (2 ml) of ketone (1 mmol) was added dropwise to a stirred THF solution of sodium 1,1,1,3,3,3-hexamethyldisilisane (1 M, 1.3 ml) cooled to 0°C. After 3 h, this mixture was added to a THF solution (10 ml) of the alkyl halide (10 mmol) cooled to -78°C. The mixture was heated slowly to room temperature and stirring was maintained for 4-7 days. The mixture was added to saturated aq. ammonium chloride. After separation of the organic phase and drying over $MgSO_4$, the product was isolated by flash-chromatography eluting with AcOEt/petroleum ether (2/98).

- 2-benzyl-2-isobutyl-(3,4)-dihydronaphthalen-1-one **1c**. Yield: 95 % (from **3b** + $PhCH_2Br$). ^{1}H NMR (400 MHz): 0.81 (3 H, d, J= 6.4), 0.87 (3 H, d, J= 6.8), 1.50 (1 H, dd, J= 14, 6), 1.60-2.02 (4 H), 2.76 (1 H, d, J= 13.4), 2.95 (2 H, m), 3.24 (1 H, d, J= 13.4), 7.13-7.25 (7 H), 7.29 (1 H, t, J= 7.8), 8.05 (1 H, d, J= 7.8). ^{13}C NMR (75 MHz): 24.2, 24.5, 24.7, 25.3, 30.4, 41.2, 43.5, 49.4, 126.2, 126.6, 127.8, 128, 128.6, 131, 132.5, 137.8, 142.8, 201.7. IR ($CHCl_3$): 3000, 2920, 1670, 1600, 1450, 1200, 930. MS, m/e (%): 91 (100), 118 (47), 131 (42), 148 (92), 160 (27), 236 (100), 292 (<1). Anal. calcd for $C_{21}H_{24}O$, C 86.26 H 8.27, Found C 86.07 H 8.75.

- 2-methyl-2-isobutenylindan-1-one **1e**. Yield: 83% (from **3a** + $ClCH_2C(Me)=CH_2$). ^{1}H NMR (250 MHz): 1.06 (3 H, s), 1.42 (3 H, s), 2.2 (1 H, d, J= 14), 2.39 (1 H, d, J = 14), 2.68 (1 H, d, J= 17.2), 3.16 (1 H, d, J= 17.2), 4.5 (1 H, wide s), 4.6 (1 H, wide s), 7.39-7.47 (3 H), 7.61 (1 H, d, J= 7.8). ^{13}C NMR (63 MHz): 23.8, 25.5, 39.3, 45.6, 48.6, 114.4, 124.2, 126.6, 127.3, 134.7, 135.6, 142.5, 152.7, 210.6. IR ($CHCl_3$): 3000, 2960, 2920, 1700, 1600, 1445, 1425, 1290, 1275, 1190, 970, 895. MS, m/e (%): 91 (18), 115

(36), 144 (100), 145 (61), 185 (10), 200 (12, M), 201 (13, M+1).

- 2-methyl-2-isobutenyl-(3,4)-dihydronaphthalen-1-one **1f**. Yield: 57 % (from **3b** + $ClCH_2C(Me)=CH_2$). ^1H NMR (250 MHz): 1.18 (3 H, s), 1.62 (3 H, s), 1.85 (1 H, dt, J= 13.9, 6), 2.10 (1 H, dt, J= 13.9, 6), 2.21 (1 H, d, J= 13.5), 2.63 (1 H, d, J=13.5), 2.93 (2 H, t, J= 6), 4.65 (1 H, wide s), 4.8 (1 H, wide s), 7.18 (1 H, d, J= 7,8), 7.28 (1 H, d, J= 7.8), 7.42 (1 H, dt, J= 7.8, 1.5), 8 (1 H, dd, J= 7.8, 1.5). ^{13}C NMR (63 MHz): 16.4, 23.2, 24.4, 25.4, 33.5, 44.7, 44.9, 111.9, 114.9, 126, 128, 128.6, 131.8, 132.9, 142.4, 143.1, 202.1. IR ($CHCl_3$): 2910, 1665, 1595, 1450, 1370, 1190, 890.

Hydrogenation of **1e** *and* **1f**. Hydrogen was bubbled at room temperature for 2 h through an ether solution (3 ml) of the ketone (1 mmol) containing PtO_2 (0,1 equiv.). After evaporation of the solvent, the residue was purified by flash-chromatography eluting with AcOEt/petroleum ether (5/95).

- 2-isobutyl-2-methylindan-1-one **1a**. Yield: 96 %. ^1H NMR (300 MHz): 0.84 (3 H, d, J= 6.3), 0.9 (3 H, d, J= 6.3), 1.2 (3 H, s), 1.50-1.77 (3 H), 2.87 (1 H, d, J= 18), 3.22 (1 H, d, J= 18), 7.37 (1 H, t, J= 7,2), 7.44 (1 H, d, J= 7.2), 7.6 (1 H, t, J= 7,2), 7.72 (1 H, d, J= 7.2). ^{13}C NMR (75 MHz): 23.6, 24.7, 25.1, 25.3, 40.4, 46.4, 49, 124.3, 126.5, 127.3, 134.7, 135.9, 152.6, 211.5. IR ($CHCl_3$): 2960, 1700, 1600, 1460, 1370. MS, m/e (%): 91 (15), 105 (15), 131 (23), 146 (100), 159 (4), 203 (5, M+1). UV (MeCN): λ_{max}= 240 nm, ε= 12260, λ_{max}= 285 nm, ε= 2580, λ_{max}= 293 nm, ε= 2530, λ_{max}= 324 nm, ε= 65. Anal. calcd for $C_{14}H_{18}O$, C 83.12 H 8.97, Found C 83.25 H 9.33.

- 2-isobutyl-2-methyl-(3,4)-dihydronaphthalen-1-one **1b**. Yield: 84 %. ^1H NMR (250 MHz): 0.88 (3 H, d, J= 6.3), 0.91 (3 H, d, J= 6.3), 1.23 (3 H, s), 1.5 (1 H, dd, J= 16, 7.8), 1.70-1.84 (1H), 1.94 (1 H, ddd, J= 13, 7, 5.7), 2.16 (1 H, ddd, J= 13, 7, 5.7), 2.90-3.34 (2 H), 7.26 (1 H, dd, J= 7.6, 0.8), 7.32 (1 H, dt, J= 7.6, 0.8), 7.47 (1 H, dt, J= 7.6, 1.2), 8.06 (1 H, dd, J= 7.6, 1.2). ^{13}C NMR (63 MHz): 23.2, 24.4, 24.5, 24.6, 25.4, 34.1, 44.9, 45.3, 126.5, 127.9, 128.5, 132, 132.8, 143, 202.8. IR ($CHCl_3$): 3010, 1670, 1600, 1450, 1375, 1310, 1200, 975. MS, m/e (%): 90 (21), 118 (31), 131 (14), 145 (31), 160 (100), 217 (3, M+1). Anal. calcd for $C_{15}H_{20}O$, C 83.29 H 9.32, Found C 83.28 H 9.56.

- 2-hydroxy-2-isobutylindan-1-one **1d**. A solution of the ketone **3e** (1.06 g, 5.64 mmol), trimethylphosphite (1.43 ml, 12.1 mmol) and tetrabutylammonium iodide (0.21 g) in toluene (68 ml) was added to stirred aq. 50% sodium hydroxide (20 ml). Oxygen was bubbled into the mixture for 16 h. After conventional workup, flash-chromatography eluting with AcOEt/petroleum ether (10/90) led to **1d** (1.02 g). Yield: 89 %. m.p.: 66 °C. ^1H NMR (300 MHz): 0.88 (3 H, d, J= 6.6), 0.96 (3 H, d, J= 6.6), 1.55 (1 H, dd, J= 14, 6.6), 1.70 (1 H, dd, J= 14, 6.6), 1.83 (1 H, m), 2.85 (1 H, s), 3.19 (1 H, d, J= 17), 3.37 (1 H, d, J= 17), 7.38 (1 H, t, J= 7.6), 7.44 (1 H, d, J= 7.6), 7.62 (1 H, t, J= 7.6), 7.77 (1 H, d, J= 7.6). ^{13}C NMR (75 MHz): 24.1, 24.3, 24.5, 40.4, 46.6, 80, 124.7, 126.6, 127.8, 134.2, 135.7, 151.5, 208.2. IR ($CHCl_3$): 3544, 3440, 2960, 1710, 1610, 1475, 1300, 1220, 1150, 1030, 940. MS, m/e (%): 57 (100), 65 (15), 77 (12), 85 (55), 91 (75), 105 (22), 115 (14), 120 (17), 130 (18), 148 (88), 161 (77), 187 (<3), 204 (<4). UV (MeCN): λ_{max}= 222 nm, ε= 870, λ_{max}= 302 nm, ε= 440. Anal. calcd for $C_{13}H_{16}O$, C 76.44 H 7.9, Found C 76.76 H 7.86.

General procedure for mono alkylation of **9**, **10a** *and* **10b**. A THF solution (25 ml) of the ketone (80 mmol) was added to a THF slurry (35 ml) of sodium hydride (81 mmol). After the gaseous emission has stopped, alkyl halide (81 mmol) was added dropwise. The mixture was heated at 60°C for 18 h, cooled to room temperature, acidified with 2 M HCl to neutral pH and then extracted as usual. The ketone was isolated by flash-chromatography eluting with AcOEt/petroleum ether (2/98).

For direct dialkylation, the reaction was carried out at room temperature using an excess of both sodium

hydride and alkyl halide (4 equiv. each).

- 1-phenyl-2-methyl-2-propylpentan-1-one **5a**. Yield: 54 % from **10a** or 71 % from **9**. ^{1}H NMR (300MHz): 0.85 (6 H, t, J= 6.7), 1.25 (3 H, s), 1.05-1.4 (4 H), 1.57 (2 H, dt, J= 13.5, 4.5), 1.85 (2 H, dt, J= 13.5, 4.5), 7.4 (3 H, m), 7.65 (2 H, m). ^{13}C NMR (75 MHz): 9.5, 14.3, 14.7, 17.8, 22.6, 42, 51.7, 127.2, 128, 130.6, 139.7, 209.3. IR ($CHCl_3$): 2950, 1665, 1465. Anal. calcd for $C_{15}H_{22}O$, C 82.52 H 10.16, Found C 82.61 H 10.15.

- 1-phenyl-2-isobutyl-2,4-dimethylpentan-1-one **5b**. Yield: 19 % from **10b** or 33 % from **9**. ^{1}H NMR (300 MHz): 0.7 (6 H, d, J= 5.5), 0.9 (6 H, d, J= 5.5), 1.3 (3 H, s), 1.5 (2 H, dd, J= 13.5, 5.5), 1.65 (2 H, octet, J= 5.5), 2 (2 H, dd, J= 13.5, 5.5), 7.45 (3 H, m), 7.76 (2 H, m). ^{13}C NMR (75 MHz): 23.3, 23.9, 24.1, 24.9, 50.1, 51.9, 128, 128.4, 130.9, 139.4, 208.5. IR ($CHCl_3$): 2950, 1670, 1590, 1470, 1080, 1040, 975. MS, m/e (%): 57 (100), 77 (36), 105 (93), 140 (24), 190 (10), 230 (9), 247 (6), 247 (6, M+1). Anal. calcd for $C_{17}H_{26}O$, C 82.87 H 10.64, Found C 83.05 H 10.95.

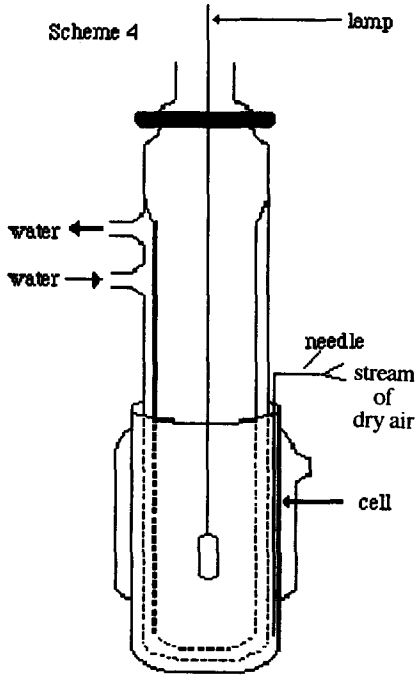
- 1-phenyl-2-methylpentan-1-one **10a**. Yield: 82 %. ^{1}H NMR (300MHz): 0.90 (3 H, t, J= 8.5), 1.20 (3 H, d, J= 6.7), 1.25-1.50 (3 H), 1.85 (1 H, m), 3.50 (1 H, sextet, J= 6.7), 7.47 (1 H, m), 7.55 (1 H, m), 7.96 (2 H, m). ^{13}C NMR (75 MHz): 14.1, 17.1, 20.5, 35.8, 40.2, 128.2, 128.5, 132.7, 136.7, 203.4. IR ($CHCl_3$): 2950, 1665, 1595, 1465, 1075, 1040, 965.

- 1-phenyl-2,4-dimethylpentan-1-one **10b**. Yield: 46 %. ^{1}H NMR (250 MHz): 0.85 (3 H, d, J= 6.6), 0.89 (3 H, d, J= 6.6), 1.14 (3 H, d, J= 6.6), 1.18-1.33 (1 H), 1.50-1.80 (2 H), 3.52 (1 H, sextet, J= 6.6), 7.55-7.36 (3 H), 7.87 (2 H, d, J= 9.7). ^{13}C NMR (63 MHz): 17.5, 22.3, 23, 25.9, 38.4, 42.7, 128.2, 128.6, 132.7, 136.7, 204.5. IR ($CHCl_3$): 2950, 1670, 1590, 1580, 1440, 1070, 1030, 970.

Irradiations

General procedure. Pyrex glass was used. The ketone and aminoalcohol (0.1 equiv.) were diluted in the solvent. Argon was bubbled into the solution for 30 mn. Irradiations were carried using either a HOQ 400 W - ($\lambda > 290$ nm) or a HPW 125 W-T- ($\lambda = 366$ nm) Philips lamp. With the first lamp, the reactor shown in scheme 4 was used. With the second lamp, the solution was contained in tubes which were placed around the reflux condenser of the lamp. For irradiations carried out at low temperatures, the temperature of the cooled bath was homogenized by stirring. Purifications of the irradiated mixtures were carried out using preparative thin layer chromatographic plates eluting with EtOAc/ petroleum ether and taking precautions to preclude enantiomer-differentiation of the isolated compounds.[27]

Scheme 4



- 2-benzyl-(3,4)-dihydronaphthalen-1-one **3c**. ^{1}H NMR (250 MHz): 1.64-1.95 (1 H), 2.00-2.25 (2 H),

2.56-2.86 (2 H), 2.86-3.09 (2 H), 3.40-3.60 (1 H), 7.10-7.38 (7 H), 8.07 (1 H, m), 7.44 (1 H, m). IR (CCl_4): 1700, 1535.

- 5,7,7-trimethyl-2,3-phenylbicyclo[3.2.0]heptan-1-ol **11**. NMR ^1H (300 MHz): 0.75 (3 H, s), 1.25 (1 H, d, J= 11.3), 1.35 (6 H, s), 1.67 (1 H, d, J= 11.3), 1.90 (1 H, wide s), 2.75 (1 H, d, J= 15.7), 2.88 (2 H, d, J= 15.7), 7.15-7.40 (4 H, m). ^{13}C NMR (65 MHz): 18.4, 21.6, 24.3, 26.8, 41.4, 44, 44.2, 47.3, 47.4, 87.3, 125.5, 125, 126.5, 128.3, 143.2, 145.4, 178.9. IR (CCl_4): 3580, 3450, 2940, 2920, 1480, 1210, 1120, 1085.

- 2-[2',4'-dimethylpent-1'-enyl] benzaldehyde **12**. 1/1 mixture of *E* and *Z* isomers. ^1H NMR (300 MHz): 0.73 (3 H, d, J= 7.5), 0.96 (3 H, d, J= 7.5), 1.62 (3 H/2, d, J= 1.4), 1.92 (3 H/2, d, J= 1.4), 1.72-1.90 (2 H), 1.88 (2 H/2, d, J= 8), 2.12 (2 H/2, d, J= 8), 6.56 (1 H/2, wide s), 6.60 (1 H/2, wide s), 7.18-7.40 (1 H), 7.50-7.58 (1 H), 7.85-7.91 (1 H), 10.24 (1 H/2, d, J= 1), 10.25 (1 H/2, d, J= 1). ^{13}C NMR (64 MHz): 17.6, 22.3, 22.5, 23.2, 26.3, 41.5, 49.6, 122, 122.4, 127.6, 127.8, 130.8, 130.9, 133.5, 192.6, 192.7. IR (CCl_4): 3400, 2960, 1700, 1600, 1210. MS, m/ e (%): 91 (70), 124 (29), 131 (42), 145 (100), 159 (20), 186 (8), 202 (3). Anal. calcd for $C_{14}H_{18}O$, C 83.12 H 8.97, Found C 82.70 H 9.07.

- 2-propenylbenzaldehyde **13**. 65/35 mixture of *E* and *Z* isomers. ^1H NMR (250 MHz): *Z* isomer: 1.70 (3 H, dd, J= 6, 1), 5.80-6.35 (2 H), 7.00-7.70 (3 H), 7.91 (1 H, d, J= 7), 10.24 (1 H, s). *E* isomer: 1.96 (3 H, dd, J= 6, 1), 5.80-6.35 (2 H), 7.00-7.70 (3 H), 7.80 (1 H, d, J= 7), 10.30 (1 H, s).

- 7,7-dimethyl-2,3-phenylbicyclo[3.2.0]heptan-1,5-diol **21**. ^1H NMR (300 MHz): 0.80 (3 H, s), 1.47 (3 H, s), 1.54 (1 H, d, J= 13.5), 1.92 (1 H, d, J= 13.5), 2.00-2.70 (2 H), 2.96 (1 H, d, J= 18), 3.13 (1 H, d, J= 18), 7.17-7.37 (4 H). ^{13}C NMR (63 MHz): 23.9, 25.6, 41, 44.9, 45.9, 78.9, 84.3, 126.2, 126.8, 127.6, 128.6, 135.9, 141.3, 143. IR ($CHCl_3$): 3560, 3000, 2960, 2930, 1600, 1080, 1040.

- 2-[4'-methyl-2'-oxopentyl]-benzaldehyde **22**. ^1H NMR (300 MHz): 0.96 (6 H, d, J= 8), 2.20 (1 H, m), 2.50 (2 H, d, J= 8), 4.15 (2 H, s), 7.21 (1 H, m), 7.43-7.60 (2 H), 7.85 (1 H, dd, J= 7.3, 1.6), 10.04 (1 H, s). ^{13}C NMR (63 MHz): 22.5, 24.3, 47.8, 51.7, 127.5, 132.5, 133.5, 134.2, 134.8, 136, 193.2, 206.7. IR ($CHCl_3$): 3600, 2960, 1690, 1465, 1380.

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REFERENCES AND NOTES

1. For reviews, see: a) Hart, H.; *Chem. Rev.* **1979**, *79*, 515; b) Kresge, A.J. *L'actualité chimique* **1988**, 233; c) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 442; d) Capon, B.; Guo, B. Z.; Kwok, F. C.; Siddhanta, A.K.; Zucco, C. *ibid.* **1988**, *21*, 135; e) Kresge, A. J. *ibid.* **1990**, *23*, 43; f) *The Chemistry of Enols* Rapoport, Z. Ed., Wiley: Chichester, 1990; g) Capon, B in *The Chemistry of Enones* Patai, S.; Rappoport, Z. Eds., Wiley: Chichester, 1989, part 2, p 1063; h) Pollack, R.M. *Tetrahedron* **1989**, *45*, 4913; i) Chiang, Y.; Kresge, A.J *Science* **1991**, *253* 395; For recent examples, see: j) Capon, B.; Guo, B.Y. *J. Am. Chem. Soc.* **1988**, *110*, 5144; k) Chiang, Y.; Kresge, A.J.; Schepp, N.P. *J. Am. Chem. Soc.* **1989**, *111*, 3977; l) Shimizu, N.;. Miyahara, T.; Mishima, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn* **1989**, *62*, 2032; m) Dzingeleski, G.D.; Blotny, G.; Pollack, R.M. *J. Org.*

Chem. **1990**, *55*, 1019; n) Nadler, E.B.; Rappoport, Z. *ibid.* **1990**, *55*, 2673; o) Keeffe, J. R.; Kresge, A.J.; Schepp, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 4862; p) Schmittel, M.; Baumann, U. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 541; q) Urwyler, B.; Wirz, J. *ibid* **1990**, *29*, 790; r) Chiang, Y.; Kresge, A. J.; Pruszynski, P.; Schepp, N. P.; Wirz, J. *ibid* **1990**, *29*, 792; s) Decicco, C.P.; Buckle, R.N. *J. Org. Chem.* **1992**, *57*, 1005; t) Kresge. A.J.; Tobin, J.B. *ibid* **1993**, *58*, 2652; u) Hajipour, G.; Johnson, W.H.; Dauben, P.D.; Stolowich, N.J.; Whitman, C.P. *J. Am. Chem. Soc.* **1993**, *115*, 3533; v) Inoue, H.; Sakurai, T.; Hoshi, T.; Okubo, J. *J. Photochem. Photobiol. A: Chem.* **1993**, *72*, 41; w) Nadler, E.B.; Rôck, M.; Schmittel, M.; Rappoport, Z. *J. Phys. Org. Chem.* **1993**, *6*, 233.

2. a) For a review, see: Duhamel, L.; Duhamel, P.; Launay, J.C.; Plaquevent, J.C. *Bull. Soc. Chim. Fr. II* **1984**, 421; b) Pracejus, H.; Rennau, R. *React. Kinet. Catal. Lett.* **1980**, *15*, 203; c) Hogeven, H.; Zwart, L. *Tetrahedron Lett.* **1982**, *23*, 105; d) Duhamel, L.; Launay, J.C. *ibid* **1983**, *24*, 4209; e) S. Takano, Kudo, J.; Takahashi, M.; Ogasawara, K. *ibid* **1986**, *27*, 2405; f) Duhamel, L.; Fouquay, S.; Plaquevent, J. C. *ibid* **1986**, *27*, 4975; g) Gerlach, U.; Hünig, S. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1283; h) Duhamel, L.; Duhamel, P.; Fouquay, S.; Eddine, J.J.; Peschard, O.; Plaquevent, J. C.; Ravard, A.; Solliard, R.; Valnot, J. Y.; Vincens, H. *Tetrahedron* **1988**, *44*, 5495; i) Fehr, C.; Galindo, J. *J. Am. Chem. Soc.* **1988**, *110*, 6909; j) Matsumoto, K.; Ohta, H. *Chem. Lett.* **1989**, 1389; k) Potin, D.; Williams, K.; Rebek, J. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1420; l) Matsumoto, K.; Tsutsumi, S.; Ihori, T.; Ohta, H. *J. Am. Chem. Soc.* **1990**, *112*, 9614; m) Fehr, C. *Chimia* **1991**, *45*, 253; n) Matsumoto, K.; Ohta, H. *Tetrahedron Lett.* **1991**, *32*, 4729; o) Fujii, I.; Lerner, R.A.; Janda, K.D. *J. Am. Chem. Soc.* **1991**, *113*, 8258; p) Kume, Y.; Ohta, H. *Tetrahedron Lett.* **1992**, *33*, 6367; q) Reymond, J.L.; Janda, K.D.; Lerner, R.A. *J. Am. Chem. Soc.* **1992**, *114*, 2257; r) Takeuchi, S.; Miyoshi, N.; Hirata, K.; Hayashida, H.; Ohgo, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2001; s) Takeuchi, S.; Miyoshi, N.; Hirata, K.; Hayashida, H.; Ohgo, Y. *Chem. Lett.* **1992**, 551; t) Fuji, K.; Tanaka, K.; Miyamoto, H. *Tetrahedron: Asymmetry* **1993**, *4*, 247.

3. An enediol was postulated as an intermediate in the course of the asymmetric protonation of the potassium enediolate of (±) benzoin,[2d] see also ref. 2r.

4. Hénin F., Muzart J., Pète J.P., M'Boungou M'Passi A., Rau H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 416.

5. a) Bergens, S.H.; Bosnisch, B. *J. Am. Chem. Soc.* **1991**, *113*, 958; b) Hénin, F.; Muzart, J. *Tetrahedron: Asymmetry* **1992**, *3*, 1161.

6. For reviews, see: a) Kagan, H.B.; Fiaud, J.C. in *Topics in Stereochemistry* Eliel, E.L.; Allinger, N.L. Eds., Wiley: New York, 1978, Vol. 10, p 175; b) Rau, H. *Chem. Rev.*. **1983**, *83*, 535; c) Inoue, Y. *Chem. Rev.*. **1992**, *92*, 741.

7. a) Hénin, F.; Mortezaei, R.; Muzart, J.; Pete, J.P. *Tetrahedron Lett.* **1992**, *33*, 1495; b) *ibid* **1985**, *26*, 4945; c) Pète, J.P.; Henin, F.; Mortezaei, R.; Muzart, J.; Piva, O. *Pure Appl. Chem.* **1986**, *58*, 1257; d) Hénin, F.: Mortezaei, R.; Muzart, J.; Pète, J.P.; Piva, O. *Tetrahedron* **1989**, *45*, 6171; e) Piva, O.; Pète, J.P.*Tetrahedron Lett.* **1990**, *31*, 5157; f) Hénin, F.; Muzart, J.; Pète, J.P.; Piva, O. *New. J. Chem.* **1991**, *15*, 611-613.

8. a) Mortezaei, R.; Awandi, D.; Hénin, F.; Muzart, J.; Pète, J.P. *J. Am. Chem. Soc.* **1988**, *110*, 4824; b) Awandi, D.; Hénin, F.; Muzart, J.; Pète, J.P. *Tetrahedron: Asymmetry* **1991**, *2*, 1101.

9. a) Mortezaei, R.; Piva, O.; Hénin, F.; Muzart, J.; Pète, J.P. *Tetrahedron Lett.* **1986**, *27*, 2997; b) Piva,

O.; Mortezaei, R.; Hénin, F.; Muzart, J.; Pète, J.P. *J. Am. Chem. Soc.* **1990**, *112*, 9263.

10. a) Mc Millan, G R.; Calvert, J.G.; Pitts, J. N. *J. Am. Chem. Soc.* **1964**, *86* 3602; b) Wagner, P.J. *Acc. Chem. Res.* **1971**, *4*, 168; c) Henne, A.; Fischer, H. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 435.
11. Furthermore, it has been shown that the photoreactivity of 2-isopropylcyclopentanone is different from that of the 2-isopropylcyclohexanone: Morizur, J.P.; Furth, B.; Kossanyi, J. *Bull. Soc. Chim. Fr.* **1970**, 1959.
12. Hughes, D.L.; Dolling, U.H.; Ryan, K.M.; Schoenewaldt, E.F.; Grabowski, E.J.J. *J. Org. Chem.* **1987**, *52*, 4745.
13. Davis, F.A.; Kumar, A.; Chen, B.C. *J. Org. Chem.* **1991**, *56*, 112.
14. a) Gardner, J.N.; Carlon, F.E.; Gnoj, O. *J. Org. Chem.* **1968**, *33*, 3294; b) Masui, M.; Ando, A.; Shioiri, T. *Tetrahedron Lett.* **1988**, *29*, 2835.
15. Jaouen, G.; Meyer, A. *J. Am. Chem. Soc.* **1975**, *97*, 4667.
16. Murakata, M.; Nakajima, M.; Koga, K. *J. Chem. Soc., Chem. Com.* **1990**, 1657.
17. a) Baum, A.A. *J. Am. Chem. Soc.* **1972**, *94*, 6866; b) Hamer, N.K. *J. Chem. Soc. Perkin Trans I* **1979**, 1285.
18. Phenanthrene: E_T = 62 Kcal.Mol^{-1}; Indan-1-one: E_T = 76 Kcal.Mol^{-1} in *Handbook of Photochemistry* Murov, S.L., Marcel Dekker: New York, 1973, p. 5 and 17.
19. Padwa, A.; Eastman, D. *J. Am. Chem. Soc.* **1969**, *91*, 462.
20. a) Wagner, P.J.; Spoerke, R.W. *J. Am. Chem. Soc.* **1969**, *91*, 4437; b) Dalton, J.C.; Dawes, K.; Turro, N.J.; Weiss, D.S.; Barltrop, J.A.; Coyle, J.D. *J. Am. Chem. Soc.* **1971**, *93*, 7213; c) Turro, N.J.; Dalton, J.C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92.
21. Lewis, F.D.; Hilliard, T.A. *J. Am. Chem. Soc.* **1970**, *92*, 6672.
22. See for examples, a) Gatechair, L.R.; Wostratzky, D. *Adhesive Chem.* **1984**, 409; b) Decker, C. *J. Coating Technology* **1987**, *59*, 97.
23. a) Butenandt, A.; Poschmann, L. *Ber.* **1944**, *77*, 394; b) Wehrli, H.; Schaffner, K. *Helv. Chim. Acta* **1962**, *45*, 385; c) Fetizon, M.; Gramain, J.C. *Bull. Soc. Chim. Fr.* **1967**, 1003; d) Tarasov, V.F.; Ghatlia, N.D.; Buchachenko, A.L.; Turro, N.J. *J. Am. Chem. Soc.* **1992**, *114*, 9517.
24. M'Boungou M'Passi, A.; Hénin, F.; Muzart, J.; Pète, J.P. *Bull. Soc. Chim. Fr.*, **1993**, *130*, 214.
25. Saavedra, J.E. *J. Org. Chem.* **1985**, *50*, 2271.
26. Tanaka, K.; Ushio, H.; Kawabata, Y.; Suzuki, H. *J. Chem. Soc. Perkin Trans*, **1991**, *1*, 1445.
27. a) Tsai, W.; Hermann, K.; Hug, E.; Rohde, B.; Dreiding, A.S. *Helv. Chim. Acta* **1985**, *68*, 2238; b) Matusch, R.; Coors, C. *Angew. Chem. Int. Ed. Engl.* **1989**, *28* , 626.

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