

Formation of β -Hydroxyketones from α, β -Epoxyketones by Photoinduced Single Electron Transfer Reactions

J. Cossy^{*a}, A. Bouzide^a, S. Ibhi^a, P. Aclinou^b

a) Laboratoire de Chimie Organique associé au CNRS, ESPCI 10 rue Vauquelin,
75231 Paris Cedex 05 - France

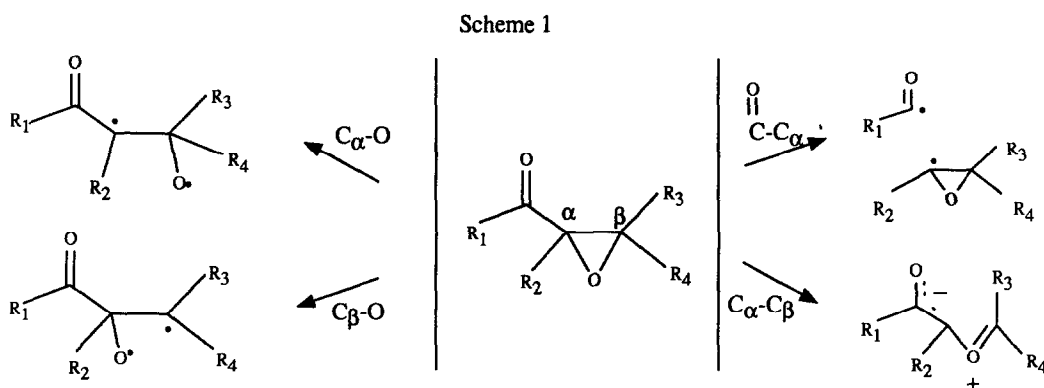
b) Laboratoire des réarrangements thermique et photochimique associé au CNRS, UFR Sciences,
Moulin de la Housse, 51062 Reims Cedex - France

(Received in Belgium 20 June 1991)

Key words α, β -epoxyketones, β -hydroxyketones, radical, photochemistry

Abstract Irradiation of α, β -epoxyketones in acetonitrile at 254 nm in the presence of triethylamine afforded β -hydroxyketones in good to moderate yields

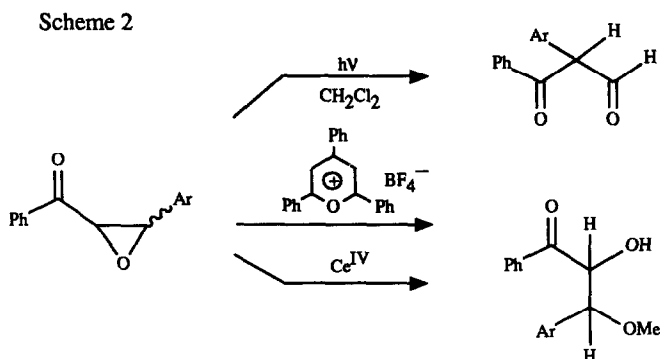
Since the discovery of β -diketone formation by irradiation of α -epoxyketones¹, extensive studies showed that more than one photochemical process can occur depending on the substitution and on the nature of the reactive excited states². While β -diketones are formed predominantly by rupture of the C_{α} -O bond from a singlet $n\pi^*$ excited state, α -diketones are the major products when the C_{β} -O bond is cleaved or when there is an aryl group in the β -position³. Epimerized epoxyketones^{4,5}, as well as fragmentation⁶ and cycloaddition products^{7,8} are isolated when the carbon-carbon bond α to the carbonyl is cleaved (Norrish type I). The C_{α} - C_{β} bond cleavage produces a carbonyl ylide intermediate that can be trapped with appropriate olefins⁹ (Scheme 1).



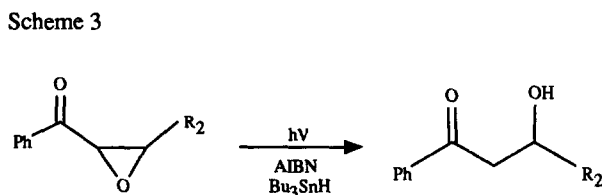
Many of the factors directing the course of the photolysis remain unclear today, although it appears that epimerization and ylide formation occur preferentially from the triplet excited state of the α -epoxyketones.

It has been shown recently that C_{β} -O bonds of chalcone epoxides can be cleaved selectively by

pyrilium salt sensitized photoreactions¹⁰ This leads to β -ketoaldehydes when CH_2Cl_2 is used as solvent and to methanol adducts when the reaction is run in methanol. Similarly and in the dark, cerium(IV) salts catalyze methanol-adduct formation from the chalcone epoxide¹⁰ (Scheme 2)



Alternatively selective $\text{C}_{\alpha}\text{-O}$ bond cleavage occurs when the α,β -epoxyketones are irradiated or heated with azoisobutyronitrile in the presence of tributyltin hydride in benzene¹¹ (Scheme 3)



In connection with our studies¹² on the chemistry of radical-anions produced photochemically by induced electron transfer onto carbonyl compounds from triethylamine, we envisaged that the irradiation of α,β -epoxyketones under these conditions might cause selective $\text{C}_{\alpha}\text{-O}$ bond cleavage. Protonation and hydrogen atom abstraction by the radical-anion intermediate would lead to the formation of β -hydroxyketones

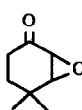
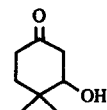
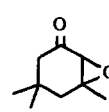
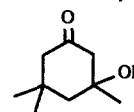
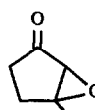
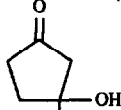
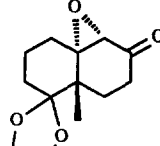
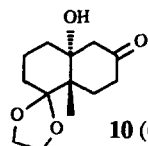
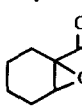
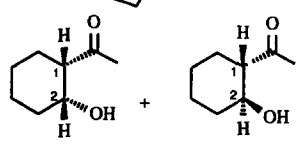
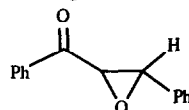
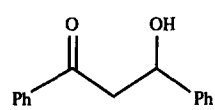
Results

The epoxyketones 1-6 were prepared from the corresponding unsaturated ketones using a mixture of hydrogen peroxide and sodium hydroxide in methanol¹³ The irradiation (low pressure mercury lamps, 254 nm, in quartz vessel) of 1-6 were performed in acetonitrile solutions containing 5 equivalents of triethylamine

The results of the reactions are summarized in Table I

The only product isolated after one hour of irradiation of 1 was the hydroxyketone 7¹⁴ (45 % yield, 50 % conversion). Prolonged irradiation of the solution resulted in the decomposition of the photoproduct 7 and led to a complex mixture which could not be analyzed. The irradiation of isophorone oxide 2 produced 3,4,4-trimethyl-3-hydroxycyclohexanone 8 with a yield of 62 % when the conversion of 2 is 80%. The photolysis of 3 in the presence of triethylamine allowed the isolation of the hydroxyketone 9 with a yield of 65 %. After one hour of irradiation of 4, in the presence of triethylamine, a 56 % conversion rate was observed and 10 is formed in 68 % yield. The photoreduction of the *trans*-chalcone epoxide 6 gave a single

Table I Photoreduction of 1-6 (3×10^{-2} M) in CH_3CN (25 °C)

Products	Irradiation	Conversion %	Products (yields %)
 1	1 hr	50 %	 7 (45 %)
 2	45 min	80 %	 8 (62 %)
 3	1 hr	85 %	 9 (65 %)
 4	1 hr	56 %	 10 (68 %)
 5	45 min	80 %	 11 (18 %) 12 (52 %)
 6	45 min	88 %	 13 (42 %)

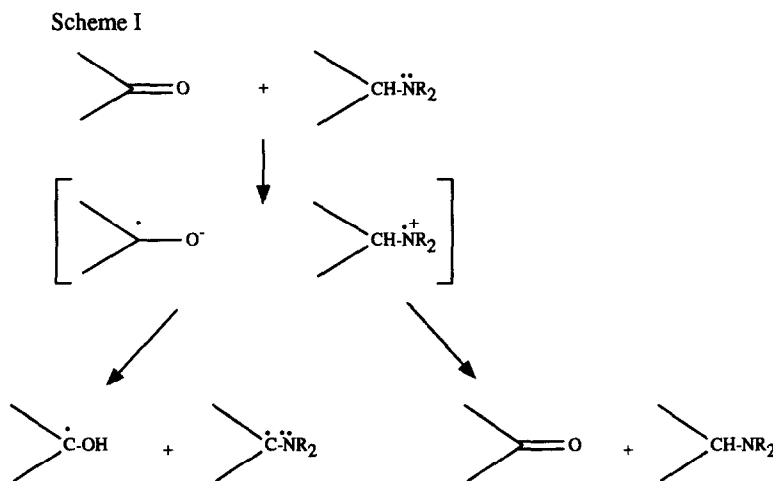
product isolated by thin layer chromatography (TLC) on silica gel, and identified as the hydroxyketone **13** (42% yield for a 80 % conversion of the starting product). On longer irradiation, decomposition of the hydroxyketones occurred. Irradiation of **5** under the standard conditions led to a mixture of two hydroxyketones **11** and **12** in a ratio 1:2:8 which could be separated by preparative TLC on silica gel. The relative configuration of the two isomers was established by ^1H NMR spectroscopy. In compound **12**, the proton H-C(2) at 3.9 ppm showed coupling constants of 10.0 Hz, 10.0 Hz and 4.5 Hz which are consistent with a *trans* configuration for compound **12**. This product is obtained with a yield of 52 %. For compound **11**, proton H-C(2) resonates at 4.2 ppm and the value of the coupling constants of 2.0 Hz, 4.0 Hz and 9.0 Hz, indicated that **11** had a *cis* configuration. This product was isolated with a yield of 18 %. The photoreduction of the *trans*-chalcone epoxide **6** gave a single product isolated by preparative thin layer chromatography (42 % yield, 88 % conversion). Decomposition of the hydroxyketone **13** was observed for longer irradiation times.

Discussion

When **1** is irradiated in the presence of triethylamine almost all the light is absorbed by the ketone **1** ($A_1/A_{Et_3N} = 2.46$, $[1] = 3 \times 10^{-2} \text{ M}$, $[Et_3N] = 0.175 \text{ M}$, $\epsilon_{254}[1] = 41$, $\epsilon_{254}[Et_3N] = 3.26$) and a fortiori for the epoxychalcone **6** where the ratio $A_6/A_{Et_3N} = 1121$ ($\epsilon_{254}[\mathbf{6}] = 21333$)

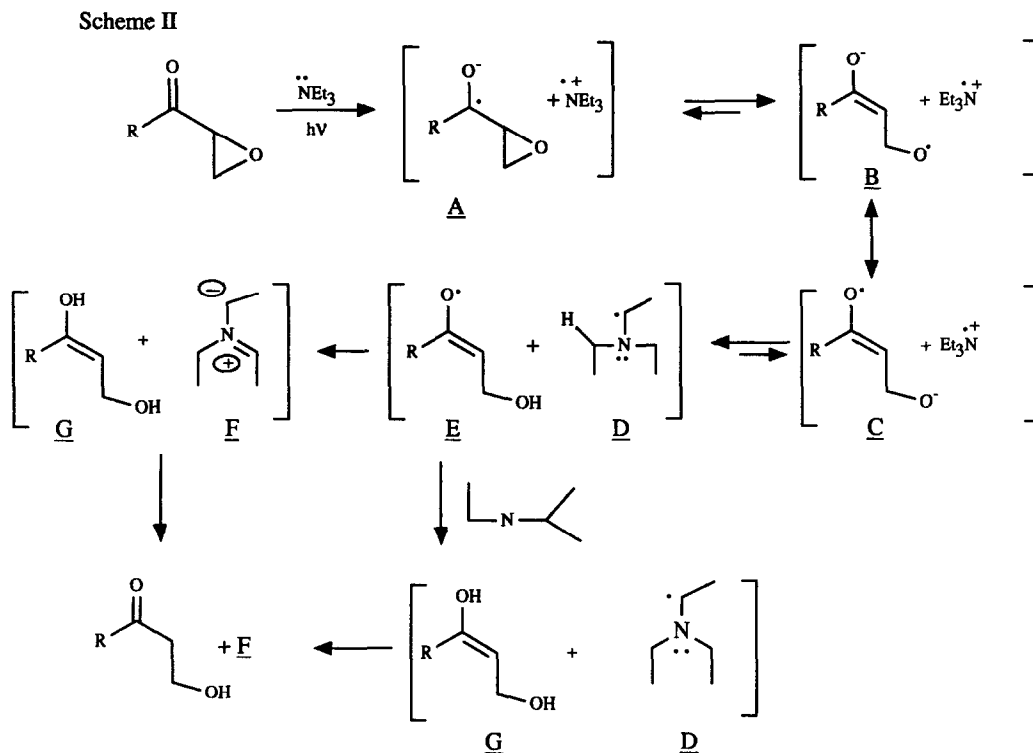
When epoxychalcone **6** was irradiated without any tertiary amine, the diketone was observed as the major product coming from an excited triplet state.^{1,15} When the irradiation of the same epoxychalcone **6** was performed in the presence of 5 equivalents of triethylamine, the diketone was no longer observed and the only product isolated was the hydroxyketone **13**. This result indicates that a single electron transfer occurs from triethylamine to **6**. The ability to transfer an electron to or from an excited molecule can be estimated by using the Rehm-Weller equation¹⁶, which gives the free enthalpy of the process, according to electrochemical parameters and the excited state energy. For an aliphatic ketones $[E(A/A^{\cdot-}) = -2.4 \text{ V/ECS} = -55.3 \text{ kcal mol}^{-1}]$ ¹⁷, the electron transfer from triplet $[E_T = 79.82 \text{ kcal mol}^{-1}]$ ¹⁸ as well as singlet excited ketone $[E_s \sim 88 \text{ kcal mol}^{-1}]$ ¹⁷ is a favored process $[\Delta G < 0]$ when triethylamine is used as an electron donor $[E(D^{\cdot+}/D) = 0.78 \text{ V/ECS} = 17.9 \text{ kcal mol}^{-1}]$ ¹⁹. For an aromatic ketone $[E(A/A^{\cdot-}) = 1.85 \text{ V/ECS} = 42.6 \text{ kcal mol}^{-1}]$ ²⁰ the singlet excited state is estimated to $E_s = 78.7 \text{ kcal mol}^{-1}$ and the triplet to $E_T = 74 \text{ kcal mol}^{-1}$ ²⁰ is also a favored process.

Cohen and coworkers have carried out extensive investigations on the photoreduction of aromatic ketones by amines.²¹ They showed that initial electron transfer to generate a radical ion pair is followed by proton transfer to give a ketyl radical and an α -aminoalkyl radical when tertiary amines are used. This radical pair can undergo back electron transfer and proton transfer to regenerate starting materials in competition with radical combination, dimerization of ketyl radicals and reaction of the α -aminoketyl radicals with ground-state ketone to give an imine and another ketyl radical (Scheme I)



In the case of epoxyketones, the formation of the hydroxyketones can be interpreted in terms of single electron transfer between the triethylamine and the ketone chromophore. This leads to ketyl radical **A** which undergoes epoxide ring opening into radical anion **B** or **C**. These two latter species might be in fact two limiting structures of the same intermediate (single minimum vs double minimum energy hypersurface). Proton transfer from $Et_3N^{\cdot+}$ to **C** gives the radical intermediates **D** + **E** which exchange an hydrogen atom and afford the intermediates **F** + **G**. Alternatively, radical **E** could abstract an hydrogen atom from Et_3N to generate **G** and the diethylaminoethyl radical **D**. In this latter case, a termination phase could also imply a

dismutation of D into triethylamine and F



The photoreductive ring opening of the α -epoxyketones is an efficient and general reaction. The advantage of our conditions is that the reactions are carried out in very mild and homogeneous conditions without any problem concerning the reproducibility, and we can obtain β -hydroxyketones very easily.

Experimental Section

General

All experiments were run under an argon atmosphere. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AC 300 instrument at 300 MHz and 75 MHz respectively, in CDCl_3 , employing Me_4Si as an internal standard. IR spectra were obtained as solutions in CHCl_3 , on a SP 3-300 Pye-Unicam spectrophotometer. UV spectra were taken on a Beckman Spectrophotometer. Mass Spectra were run on a Kratos M 50 spectrometer at 70 eV at the ICSN/CNRS of Gif-sur-Yvette. Preparative TLC was conducted on Merck silica Kieselgel 60, PF₂₅₄₊₂₆₆ and flash chromatography was accomplished with Merck silica 0 043-0 063 mm.

Preparative irradiations were conducted in a merry-go-round type system equipped with 12 low-pressure mercury Philips TUV15 lamps (254 nm), 10 mm o.d. quartz tubes were used. The solutions were degassed by bubbling argon for 15 min. Solvents such as ether and THF were distilled from sodium benzophenone. Acetonitrile and triethylamine were distilled from CaH_2 .

Preparation of epoxyketones

A typical experiment is described. To a well-stirred MeOH (5 ml) solution of enone (3.5 mmol)

cooled in a ice bath was added dropwise a mixture of H₂O₂ 30 % (2.4 ml) and a solution 6 N NaOH (0.4 ml) in methanol (4 ml). The mixture was stirred for 2 hours at 0 °C, and then 1 hour at room temperature, the reaction mixture was diluted with water (100 ml) and extracted with ethyl acetate (3x100 ml). The combined extracts were washed with brine, dried over anhydrous MgSO₄, filtered and concentrated. Purification of the crude material by flash chromatography afforded pure products.

Irradiation of epoxyketones with triethylamine

A solution of epoxyketone in dry acetonitrile (3x10⁻² M) was deoxygenated by argon bubbling. Triethylamine (5 eq) was added, and the solution was irradiated at 254 nm. Acetonitrile and triethylamine were distilled off, and the crude product was purified by preparative TLC or by flash chromatography. The reaction can be carried out on a 1 or 2 g scale.

4,4-Dimethyl-2,3-oxabicyclo[4.1.0]heptanone (1)

IR (CHCl₃) 1710, 1474, 1413, 1249, 1020, 856 cm⁻¹ *¹H NMR* (CDCl₃) 1.10 (s, 3H), 1.20 (s, 8H), 1.30-1.40 (m, 1H), 1.80-2.00 (m, 1H), 2.10-2.30 (m, 1H), 2.30-2.50 (m, 1H), 3.20 (d, J = 7 Hz, 1H) *¹³C NMR* (CDCl₃) 22.57, 27.14, 29.59, 30.46, 32.87, 55.58, 59.99, 63.78, 160.07, 205.80 *MS* m/e = 140 (20%), 99 (100%) *UV* (CH₃CN) ε₂₉₅^{max} = 287, ε₂₅₄ = 41, ε₁₉₈^{max} = 2091.

4,4-Dimethyl-3-hydroxycyclohexanone (7)

IR (CHCl₃) 3510, 1711, 1453, 1262, 1050 cm⁻¹ *¹H NMR* (CDCl₃) 1.10 (s, 3H), 1.15 (s, 3H), 1.40-1.60 (m, 1H), 1.80-1.90 (m, 1H), 2.20 (br s, 1H); 2.30-2.50 (m, 1H), 2.60-2.70 (m, 1H), 3.70 (dd, J = 4.2 Hz, J = 7.5 Hz, 1H) *¹³C NMR* (CDCl₃) 21.06, 26.04, 34.14, 34.63, 37.70, 46.37, 200.8 *MS* m/e = 142 (52%), 124 (100%) *Microanalysis* Calculated C 67.57, H 9.92, found C 67.53, H 9.88

3,5,5-Trimethyl-2,3-oxabicyclo[4.1.0]heptanone (2)

IR ((CHCl₃) 1750, 1405, 1250, 1195, 1025, 800 cm⁻¹ *¹H NMR* (CDCl₃) 0.95 (s, 3H), 1.15 (s, 3H), 1.60-1.90 (m, 2H), 2.10 (d, J = 15 Hz, 1H), 2.75 (d, J = 15 Hz, 1H) 3.10 (s, 1H) *¹³C NMR* (CDCl₃) 23.98, 27.79, 30.77, 36.14, 42.70, 61.39, 64.33, 208.17 *MS* m/e = 154 (29%), 138 (100%) *UV* (CH₃CN) ε₂₉₅^{max} = 295, ε₂₅₄ = 54, ε₁₉₈^{max} = 1050

3,5,5-Trimethyl-3-hydroxycyclohexanone (8)

MP 105 °C *IR* (CHCl₃) 3448, 1711, 908 cm⁻¹ *¹H NMR* (CDCl₃) 1.12 (s, 3H), 1.25 (s, 3H), 1.60 (br, s, 1H), 1.75 (m, 2H), 2.25 (s, 2H), 2.40 (s, 2H) *¹³C NMR* (CDCl₃) 28.31, 32.30, 33.00, 35.42, 49.88, 53.77, 53.90, 74.73, 211.04 *Microanalysis* Calculated C 74.96, H 8.38, found C 75.01, H 8.41

3-Methylbicyclo[3.1.0]hexanone (3)

IR (CHCl₃) 1750, 1405, 1210, 1050, 800 cm⁻¹ *¹H NMR* (CDCl₃) 1.50 (s, 3H), 1.85-2.50 (m, 4H), 3.10 (s, 1H) *¹³C NMR* (CDCl₃) 17.76, 27.56, 32.71, 61.06, 65.72, 210.66 *MS* m/e = 112 (10%), 57 (100%) *UV* (CH₃CN) ε₂₉₀ = 256, ε₂₅₄ = 85, ε₁₉₅ = 1860

3-hydroxy-3-methylcyclopentanone (9)

IR (CHCl₃) 3520, 1740, 1260 cm⁻¹ *¹H NMR* (CDCl₃) 1.50 (s, 3H), 1.90-2.60 (m, 7H) *¹³C NMR* (CDCl₃) 27.76, 36.74, 36.75, 53.05, 75.89, 218.36 *MS* m/e = 114 (27%), 96 (100%)

***Trans*-1,2-epoxy-7,7-ethylenedioxy-6-methylbicyclo[4.4.0]decan-3-one (4)**

MP = 135 °C *IR* (CHCl₃) 1710, 1570, 1550, 1260, 1240, 1170, 1130, 1070 cm⁻¹ *¹H NMR* (CDCl₃) 1.20 (s, 3H), 1.40-2.40 (m, 10H), 3.00 (s, 1H), 3.70-4.00 (m, 4H) *¹³C NMR* (CDCl₃) 19.97, 21.45, 25.20, 29.38, 29.99, 34.32; 63.03, 63.04, 65.25, 113.39, 164.13, 199.98 *MS* m/e = 238 (2%),

99 (100 %) *UV* (CH_3CN) : $\epsilon_{330}^{\text{max}} = 45$, $\epsilon_{254} = 50$, $\epsilon_{224}^{\text{max}} = 432$

***Trans*-1-hydroxy-7,7-ethylenedioxy-6-methylbicyclo[4.4.0]decan-3-one (10)**

IR (CHCl_3) 3520 , 1701 , 1468 , 1250 , 1150 , 1120 , 1070 , 950 cm^{-1} *¹H NMR* (CDCl_3) 1 20 (s, 3H) , 1 40-2 80 (m, 13H) , 3 80-4 20 (m, 1H) *¹³C NMR* (CDCl_3) 16 16 ; 27 42 ; 28 04 , 32 59 , 35 69 , 44 25 , 50 66 , 64 00 , 64.94 , 76 00 , 114 02 , 198 87 *MS* *m/e* = 240 (30 %) , 99 (100 %) *Microanalysis*
Calculated C 64 97 , H 8 38 , found C 64 01 , H 8 41

1-Acetyl-1,2-oxabicyclo[4.1.0]cycloheptane (5)

IR (CHCl_3) 1710 , 1435 ; 1355 , 1173 , 1138 , 856 ; 770 cm^{-1} *¹H NMR* (CDCl_3) 1 20-2 60 (m, 8H) , 2 50 (s, 3H) , 3 40 (dd, *J* = 3 Hz, *J* = 1.5 Hz, 1H) *¹³C NMR* (CDCl_3) 18.66 , 19 17 , 21 92 , 24 14 , 56 77 , 62 80 , 140 70 *MS* *m/e* = 140 (13 %) , 43 (100 %) *UV* (CH_3CN) $\epsilon_{290}^{\text{max}} = 205$, $\epsilon_{254} = 47$, $\epsilon_{230}^{\text{max}} = 2057$

***Cis*-1-acetyl-2-hydroxycyclohexane (11)**

IR (CHCl_3) 3410 , 1703 , 1450 , 1356 , 1066 cm^{-1} *¹H NMR* (CDCl_3) 1 20-2 60 (m, H) , 2 20 (s, 3H) , 4 20 (ddd, *J* = 2 0 Hz, *J* 4 0 Hz, *J* = 9 0 Hz, 1H) *¹³C NMR* (CDCl_3) 19 73 , 23 25 , 25 30 , 28 73 , 31 84 , 53 88 , 66 19 , 190 61 *MS* *m/e* = 142 (35 %) , 71 (100 %).

***Trans*-acetyl-1,2-hydroxycyclohexane (12)**

IR (CHCl_3) 3415 , 1698 , 1450 , 1356 , 1070 , 973 cm^{-1} *¹H NMR* (CDCl_3) 1 00-2 40 (m, 10H) , 2 20 (s, 3H) , 3 80 (ddd, *J* = 10 0 Hz, *J* = 10 0 Hz, *J* = 4 5 HZ, 1H) *¹³C NMR* (CDCl_3) 19 70 , 24 38 , 25 68 , 25 39 , 27 90 , 33 61 , 58 89 , 70 68 , 190 61 *MS* *m/e* = 142 (20 %) , 43 (100 %)

***Trans*-epoxychalcone (6)**

IR (CHCl_3) 1688 , 1600 , 1580 , 1450 , 1420 , 1300 , 1240 , 900 cm^{-1} *¹H NMR* (CDCl_3) 2 00 (d, *J* = 1 8 Hz, 1H) , 2 30 (d, *J* = 1 8 Hz, 1H) , 5 20-6 20 (m, 10H) *¹³C NMR* (CDCl_3) 59 03 , 60 59 , 125 49 , 127 99 , 128 10 , 128 42 , 128 52 , 128 70 , 129 79 , 129 81 , 133 32 ; 133 66 , 135 07 , 135 15 , 192 73 *MS* *m/e* = 224 (30 %) , 77 (100 %) *UV* (CH_3CN) $\epsilon_{320}^{\text{max}} = 75$, $\epsilon_{254} = 21333$, $\epsilon_{246}^{\text{max}} = 23578$, $\epsilon_{190}^{\text{max}} = 37052$

1,3-Diphenyl-1-hydroxypropanone (13)

IR (CHCl_3) 3510 , 1680 , 1450 , 754 , 700 cm^{-1} *¹H NMR* (CDCl_3) 3 30-3 40 (m, 2H) , 5 30 (dd, *J* = 7 Hz, *J* = 5 5 Hz, 1H) , 7 00-8 00 (m, 10H) *¹³C NMR* (CDCl_3) 47 33 , 69 98 , 125 70 , 127 38 , 127 61 , 128 10 , 128 50 , 128 52 , 128 63 , 128 65 , 133 58 , 136 53 , 200 08 *MS* *m/e* = 226 (46 %) , 105 (100 %)

Acknowledgments We thank Dr O Laprévotte from the ICSN/CNRS of Gif-sur-Yvette for the registration of Mass Spectra

Références

- 1 Bodforss J , *Chem Ber*, **1918**, *51*, 214
- 2 a) Nastasi M , Streith J Rearrangements in ground and excited states , de Mayo P , Ed , Academic Press New York, **1980** , Vol 3, p 445 b) Padwa A , *Organic Photochemistry* , Chapman O L , Ed , Marcel Dekker New York, **1967**, Vol 1, p 91. c) Bertoniere N R , Griffin G W , *Organic Photochemistry* Chapman O L , Ed , Marcel Dekker New York, **1973** , Vol 3, p 115

- 3 a) Pappas S P, Muller M J, Gresham R M, *J Am Chem Soc.*, **1970**, *92*, 5797 b) Pappas S P, Bao L Q, *J Am Chem Soc.*, **1973**, *95*, 7906
- 4 Johnson C K, Domny B., Reusch W, *J Am Chem Soc*, **1963**, *85*, 3894
- 5 a) Wuthrich H.J, Stevinski A, Schaffner K, Jeger O, *Helv Chim Acta*, **1973**, *56*, 239 b) Muzart J, Pète J P, *Tetrahedron Lett*, **1973**, *303*, 307.
- 6 a) Zimmerman H E, Cowley D.N., Tseng C.Y, Wilson J.W., *J Am Chem Soc*, **1964**, *86*, 947
- 7 a) Ullman E F, Henderson W A, *J Am Chem Soc*, **1966**, *88*, 4942. b) Kato H, Yamaguchi K, Tezuka H, *Chem Lett*, **1974**, 1089 c) Maruyama K, Arakawa S, Oysuki T, *Tetrahedron Lett*, **1975**, 2433 d) Arakawa S, *J Org Chem.*, **1977**, *42*, 3800. e) Kato H, Tezuka H, Yamaguchi K, Nowada K, Nakamura Y, *J Chem Soc, Perkin Trans 1*, **1978**, 1029 f) Maruyama K, Osuka A, *Chem Lett*, **1979**, *77*, *J Org Chem*, **1980**, *45*, 1898 g) Maruyama K, Arakawa S, *ibid*, **1977**, *42*, 3793
- 8 Lee G A, *J Org Chem*, **1978**, *43*, 4256
- 9 a) Hallet P., Muzart J., Pète J P, *Tetrahedron Lett*, **1979**, 2727 b) Hallet P., Muzart J, Pète J P, *J Org Chem*, **1981**, *46*, 4275
- 10 Hasegawa E, Ishiyama K, Kashiwazaki H., Horaguchi T, Shimizu T., *Tetrahedron Lett*, **1990**, *31*, 4045
- 11 a) Hasegawa E, Ishiyama K., Horaguchi T, Shimizu T., *J Chem Soc, Chem Comm*, **1990**, 550 b) Hasegawa E, Ishiyama K, Kashiwazaki H., Horaguchi T, Shimizu T, *Tetrahedron Lett*, **1990**, *31*, 4045
- 12 Belotti D, Cossy J, Pète J P, Portella C, *J Org Chem*, **1986**, *51*, 4196
- 13 Wasson R L, House H O, *Org Synth IV*, **1963**, 552
- 14 Cossy J, Aclinou A, Bellosta V, Furet N, Baranne-Lafont J, Sparfel D, Souchaud C, *Tetrahedron Lett*, **1991**, *32*, 1315
- 15 a) Padwa A, Eisenhardt W, *J Am Chem Soc*, **1970**, *92*, 1302 b) Lee G A, *J Org Chem*, **1978**, *43*, 4256.
- 16 a) Rehm D, Weller A, *Isr J Chem*, **1970**, *8*, 259 b)

$$\Delta G = 23.06 \left(E_{D/D^+} - E_{A/A^+} - \frac{e_0^2}{\epsilon_x} \right) - \Delta E_{00}, \quad \frac{e_0^2}{\epsilon_x} = 0.06 \text{ in acetonitrile}$$

- 17 Handbook series in Organic Electrochemistry, CRC Press, Boca Raton, **1982**, vol. 5
- 18 Handbook of Photochemistry, Murov, S L, Ed, Marcel Dekker Inc New York, **1973**
- 19 Hub W, Schneider S, Dorr F, Oxman J D, Lewis F D, *J Am Chem Soc* **1984**, *106*, 701
- 20 Meites L, Zuman P, CRC Handbook series in Organic Electrochemistry, CRC Press, Cleveland, **1976**, vol 1
- 21 a) Shai I, Linschitz H, Cohen S G, *J Am Chem Soc*, **1981**, *103*, 1048 b) Cohen S G, Parola A, Parsons G.H. Jr, *Chem Rev*, **1973**, 141