Tetrahedron Letters,Vol.23,No.29,pp 2981-2984,1982 0040-4039/82/292981-04$03.00/0
Printed in Great Britain

PHOTOCHEMICAL SYNTHESIS OF DIALKOXY- AND DIACETOXY-DIHYDRO-FURANS FROM TRANS-ENEDICARBONYL COMPOUNDS

R Antonioletti, M D'Auria, G Piancatelli, S Santucci, A Scettri

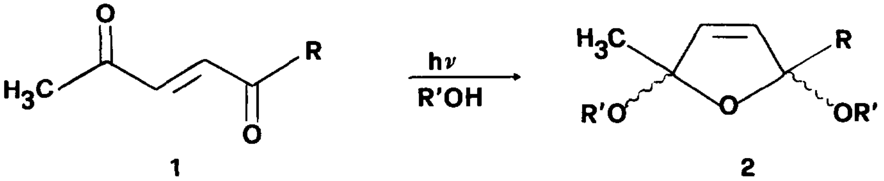
Centro CNR per lo Studio della Chimica delle Sostanze Organiche Naturali c/o
Istituto di Chimica Organica dell'Università, P le A Moro, 2 - 00185 Roma
Italy

Abstract we describe a new and efficient synthesis of the title compounds, directly obtained by photochemical alkoxilation or acetoxilation of trans-enedicarbonyl compounds A possible mechanism is discussed

2,5-Dialkoxy- and 2,5-diacetoxy-2,5-dihydrofurans have been widely used for syntheses, consisting of intermolecular or intramolecular condensations, leading to pyridazines, tropinones, pyridinols and benzenoid compounds[1] More recently, several Authors have shown their utility in the cyclopent-2-enone synthesis, as precursors of cis-enedicarbonyl compounds[2] On the contrary, only few methodologies are described for their preparation, based generally on the same procedure the chemical[2a,3,4] or electrochemical[2d,3,5] 1,4-alkoxilation or acetoxilation of furans These methods bear some disadvantages, as varying yields, formations of side products, or poor utility for substituted furans[1]

In this paper we wish to report a new and original synthesis of the title compounds, directly obtained from trans-enedicarbonyl compounds 1 They were easily prepared by our previous procedure[6], through an oxidative ring fission of furans with PCC (90 - 95%)

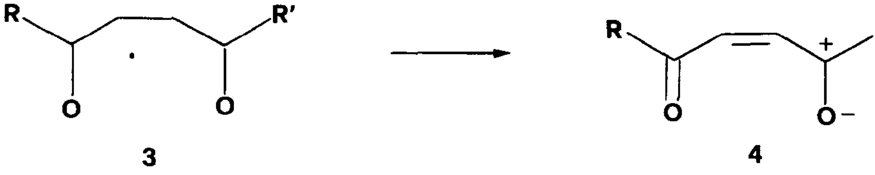
In a study designed to broaden the synthetic utility of 1, we have found that the compounds 1 undergo a photochemical alkoxilation yielding directly 2 In a typical reaction, 0 5 g of 1, dissolved in 300 ml of anhyd MeOH, were irradiated with an immersion apparatus, under N_2 The light source was a Hanovia 100-W medium pressure mercury arc sorrounded by a quartz water jacket After 4 hrs, the solvent was evaporated under reduced pressure and the residue dissol ved in Et_2O The solution was dried over Na_2SO_4 and the solvent evaporated (Table 1)



As a means of shedding light on photochemical phenomena, two major variables were investigated the nature of the medium and the type of the alcohol In these experiments, 80 mg of 1b, dissolved in 5 ml of a solvent, were irradiated with a 100-W medium pressure Hg arc, in a pyrex flask, under N_2 At the end of the reaction, the mixture was dissolved in 30 ml of Et_2O, and the solution washed several times with brine The organic layer was dried over Na_2SO_4 and the solvent evaporated (Table 2) It was possible to see the photochemical reaction worked only with MeOH, EtOH, and AcOH, the reaction was unsuccessful both in different alcohols (entries 3, 4, and 5) and in mixed protic solvents (entries 6 and 7) Furthermore, the reaction ran also in presence of a triplet quencher, naphthalene, while the irradiation of γ-diketones (i e acetonylacetone) did not produce any reaction Finally, while the known formation of ketals via an acid catalysed reaction of ketones with MeOH can be prevented by addition of solid Na_2CO_3,[7] on the contrary the conversion 1 ⟶ 2 occurred in the presence of Na_2CO_3 too

In order to explain this behaviour, we have followed the kinetics of the conversion 1 ⟶ 2 in MeOH (figure 1) and in EtOH (figure 2) by GLC While in MeOH the reaction seems to follow a zero order kinetics, in EtOH shows a more complex plot (a sigmoid curve) This difference could be only apparent, because the zero order plot of the reaction in MeOH can be considered as a very "particular" sigmoid curve

All these data allow to advance the hypothesis that the rate determining step is the reaction of a zwitterionic intermediate 4 (obtained from 3 via an



electron demotion) with the solvent

In fact, the reaction rate increases with Y-values, showing to depend on the ionizing power of the solvent, while the first part of the kinetical behaviour in

Table 1

Substrate	R	Solvent	Reaction time (h)	Product	R'	Isolated yield (%)
1a	n-C_8H_{17}	MeOH	4	2a[a]	CH_3	96
1b	n-$C_{10}H_{21}$	MeOH	4	2b[a]	CH_3	98
1c	n-$C_{12}H_{25}$	MeOH	4	2c[a]	CH_3	98

a) 2a IR (film) 1630, 1168, 1120, 1053, NMR (CCl_4, δ) 5 78, 3 20, 3 15, 3 12, 3 08, 1 48, 1 40, 1 28, 0 90, MS (m/e) 256 (M^+), 2b IR (film) 1640, 1176, 1128, 1059, NMR (CCl_4, δ) 5 78, 3 19, 3 15, 3 12, 3 06, 1 47, 1 40, 1 28, 0 88, MS (m/e) 284 (M^+), 2c IR (film) 1645, 1176, 1130, 1059, NMR (CCl_4, δ) 5 77, 3 20, 3 15, 3 13, 3 07, 1 49, 1 40, 1 28, 0 89, MS (m/e) 312 (M^+)

Table 2

Entry	Solvent	Y^8	Reaction time (h)	Product	R'	Isolated yield (%)
1	MeOH	-1 090	8	2b	Me	98
2	EtOH	-2 033	16	2d[a]	Et	84
3	i-PrOH	-2 730	8	-[b]	-	-
4	n-BuOH	------	8	-[b]	-	-
5	CH_2=$CHCH_2OH$	------	8	-[b]	-	-
6	DMF - MeOH 8 2	------	8	-[b]	-	-
7	EtOH-H_2O 8 2	0 000	8	-[b]	-	-
8	AcOH	-1 639	12	2e[c]	Ac	80

a) 2d IR (CCl_4, 1%) 1610, 1160, 1130, 1050, NMR (CCl_4, δ) 5 73 (m, 2 H), 3 00 - 3 80 (m, 4 H), MS (m/e) 312 (M^+)

b) In these cases enedicarbonyl compounds are recovered

c) 2e IR (CCl_4, 1%) 1740, 1610, 1123, 1068, NMR (CCl_4, δ) 5 56 - 6 30 (m, 2 H), 2 00 - 2 30 (m, 6 H), MS (m/e) 340 (M^+)

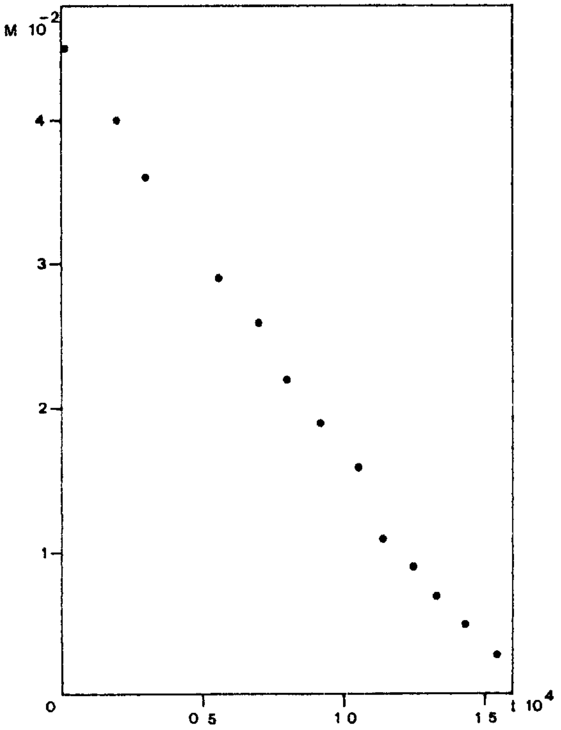


Figure 1

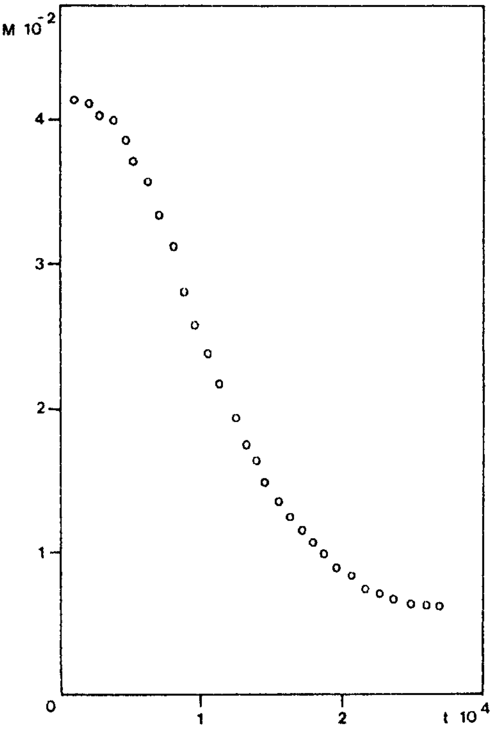


Figure 2

EtOH is distinctive for reactions of type $A \rightleftarrows B \rightarrow C$ Furthermore, the equilibrium, observed at the end of the reaction in EtOH, can be explained considering the water is able to catalyse the hydrolysis of 2[9]

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(Received in UK 11 May 1982)