STEREOCHEMISTRY OF DECARBALKOXYLATION OF ARYLMETHYLENE-PROPANEDIOIC ACIDS DIMETHYL ESTERS

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<u>Abstract</u> : Halide ions increase the rate of decarbalkoxylation of arylmethylene-propanedioic acids dimethyl esters.

In a recent paper R.V. Venkateswaran (1) reported the decarbalkoxylation of alkylidene cyano-esters. To our knowledge this is one of the few papers dealing with the decarbalkoxylation of alkylidene esters using the Krapcho (2) experimental conditions. Whereas the synthetic and the mechanistic aspects of this reaction have been widely studied, the stereochemistry of the decarbalkoxylation has so far received scant attention. Recently Krapcho (3) has studied the stereochemistry of the decarbalkoxylation of 2-methyl-1,1-cycloexanedicarboxylates using the LiCl-H_0-DMSO system. He reported for the monoesters a cis to trans ratio of 60:40.

With the aim of extending the studies on the stereochemistry of this reaction we now report the results of the decarbalkoxylation of few representative arylmethylene-propanedioic acids dimethyl esters (aryl = phenyl-, 2-methyl- and 2-methoxy phenyl). The substrates were reacted for six hours in DMSO solution using a set of different halides or potassium cyanide. Yields are in the range of 50-75% excluding the variable amounts of starting aldeyde. The stereochemical assignements were made on the basis of NMR and GLC measurements.

As the table reveals the decarbalkoxylation is highly stereoselective when the reaction is carried out in wet or dry DMSO in the presence of stoichiometric amounts of chloride ions (NaCl, LiCl) or potassium cyanide leading to the trans cinnamic ester derivatives. The use of bromide or iodide ions in wet DMSO led instead to a mixture of cis and trans-cinnamic ester derivatives in the average ratio of 20:80, but when the reaction carried out in dry DMSO only the trans-cinnamic acid was obtained (4). In the absence of halide ions the reaction gave low yields (33%) of trans cinnamic ester derivatives using dry DMSO (reaction temp. 190°C) while no decarbalkoxylation occurred when wet DMSO (reaction temp. 160°C) was used.

The use of a 10 to 1 molar ratio of diester to NaCl led the same yields of decarbalkoxylation, indicating that the effect of NaCl is catalytic. From our results it follows that the rate of decarbalkoxylation is dependent on the presence of the halide ion, whereas the stereochemistry of the reaction is related to the kind of

$C_{65}H = C(COOCH_3)_2 - C_{65}H = CHCOOCH_3 + CO_2 + CH_3OH_3$				
REACTION MEDIA	TEMP.	% YIELD	% CIS-TRANS	% STARTING ALDEYDE
DMSO	190	33	0:100	traces
DMSO-H ₂ 0 ^b	160	—	_	12,7
DMSO-H_O-NaCl	160-165	68,5	0:100	23,4
DMSO-H2O-NaC1	160-165	82	0:100	28
DMSO-NaCl	190	75,5	0:100	_
d DMSO-NaBr	190-100	95 ^d	0:100 ^d	traces
DMSO-H_O-NaBr	160-165	75,5	20:80	32
DMSO-NaI	190-100	95 ^d	0:100 ^d	traces
DMSO-H_O-NaI	160-165	82	22:78	26,5
DMSO-H_O-LiC1	160-165	68,5	0:100	28
DMSO-H_O-KCN	160-165	14	0:100	30

(a) Only results obtained for the unsubstituted derivative are reported. The <u>orto</u> substituents do not affect the yields and the stereochemistry of the reaction. (b) No detectable decarbalkoxylation. (c) 0,0045 moles diester, 0,00045 moles NaCl, 0,10 moles of water in 25 ml DMSO. (d) Initial and final reaction temperature are indicated. Trans cinnamic acid was isolated.

halogen that has been used and in the case of browide and iodide to the reaction media.

Further work is in progress to ascertain the mechanism of this reaction and to study stereochemistry of the decarbalkoxylation of different substrates.

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REFERENCES AND NOTES

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2) A.P. Krapcho, J.F. Weimaster, J.M. Eldridge, E.G.E. Jahngen, Jr. and W.P. Stephens, <u>J. Org. Chem. 43</u>, 138 (1978).

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4) When the refluxing temperature (190°C) was reached a very violent emission of CO₂ occurred; then the reaction temperature started to decrease and the pH turned immediately acid.

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TABLE^a