

THE DECARBETHOXYLATION OF GEMINAL DICARBETHOXY COMPOUNDS

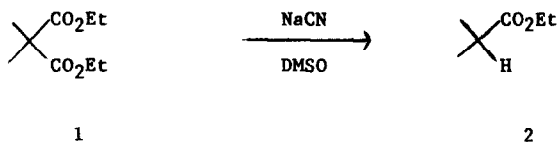
A. Paul Krapcho, Gary A. Glynn and Brian J. Grenon

Department of Chemistry, The University of Vermont

Burlington, Vermont 05401

(Received 14 November 1966)

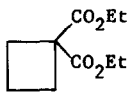
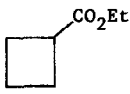
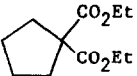
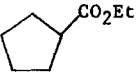
We wish to report a novel synthetic procedure for the conversion of geminal dicarbethoxy compounds to the corresponding ethyl esters 2. This decarbethoxylation can be effected by reaction of 1 with sodium cyanide in dimethyl sulfoxide (di-n-butyl sulfoxide was utilized in one run) at about 160° for 4 hours and then distillation of the crude product 2 from the reaction mixture.



This method has the advantage of comparative simplicity and produces higher overall yields than the classical procedure which involves saponification of 1 to the diacid, decarboxylation of the diacid¹ and esterification of the acid to 2.

The results of several reactions performed with variation of the cyanide concentration to ascertain the scope of this decarbethoxylation procedure are summarized in Table I.

TABLE I
DECARBETHOXYLATION OF 1,1-DIESTERS WITH SODIUM CYANIDE IN DMSO

<u>REACTANT</u> ^a	<u>PRODUCT</u>	<u>YIELD</u>
$\text{CH}_3\text{CH}(\text{CO}_2\text{Et})_2$	$\text{CH}_3\text{CH}_2\text{CO}_2\text{Et}$	75 ^b
$\text{CH}_3\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$	80 ^c ; 58 ^d ; 25 ^e
		75 ^c ; 65 ^f
		60 ^g ; 75 ^h

^a The general procedure involved heating the mixture in an oil bath at 160° for four hours and then the product and some DMSO were distilled. Cold water was added to the distillate, the product extracted into pentane, the pentane extracts washed with water and dried over sodium sulfate. The ester was isolated by distillation. The products were identified by boiling point and infrared comparisons.

^b 1 M diester and 1.5 M NaCN.

^c 0.5 M diester and 1.0 M NaCN.

^d 0.5 M diester and 0.5 M NaCN.

^e 0.5 M diester and 0.05 M NaCN. The mixture was heated at 160° for 18 hours and 60% starting material was recovered.

^f 0.5 M diester and 1.4 M NaCN in di-*n*-butyl sulfoxide. The crude product distilled from this higher boiling sulfoxide.

^g 0.25 M diester and 0.5 M NaCN.

^h 0.25 M diester and 2.5 M NaCN. The yield is crude product.

From the tabulated data it can be seen that good yields of esters can be obtained from this procedure when at least one equivalent of sodium

cyanide is utilized. Since compounds of type 1 are readily accessible, this procedure should find general utilization for the synthesis of esters.

The study of the mechanism of this decarbethoxylation is under active investigation and the procedure is being extended to other diesters and to those compounds containing ester groups which on saponification readily decarboxylate.

Acknowledgment.- The authors are indebted to the National Institutes of Health (5 RO1-GM-8241-05) and to the National Sciences Foundation (Undergraduate Research Participation Grant) for financial support which made this research possible.

REFERENCES

1. For the saponification and decarboxylation of 1,1-dicarbethoxycyclobutane see: a) J. Cason and C. F. Allen, J. Org. Chem., 14, 1036 (1949) and b) G. B. Heisig and F. H. Stodola, Org. Syntheses, Coll. Vol. 3, 312 (1955).