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THE REACTION OF TETRAMETHOXYETHYLENE WITH β-DICARBONYL COMPOUNDS

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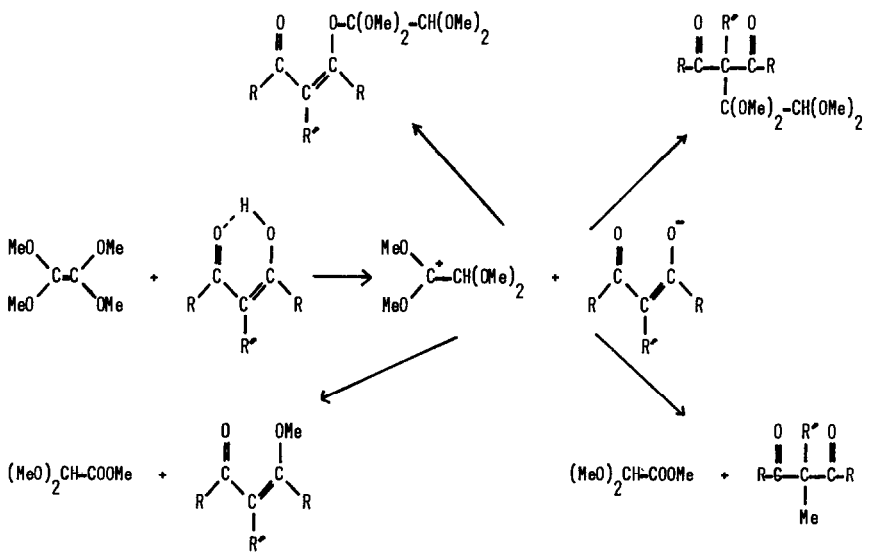
Tetramethoxyethylene (TME) is a highly nucleophilic alkene that reacts with methanol, malononitrile or benzoic acid to give the addition products, pentamethoxyethane, 1,2,2-trimethoxyethylidenemalononitrile and 1,1,2,2-tetramethoxyethyl benzoate respectively[1]. Moreover, the last product decomposes thermally to give methyl benzoate and methyl dimethoxyacetate[1].

According with these facts, the reaction of TME with β-dicarbonyl compounds can give the reaction products indicated in Scheme 1



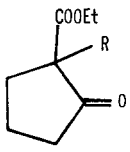
Scheme 1

Heating in a sealed NMR tube (argon atmosphere) different β-dicarbonyl compounds with TME (1:1.1 equivalents) in the absence of catalysts at temperatures between 100º and 130º for 0.5 to 115 h we have observed all the reactions indicated in Scheme 1 as shown in Table 1. Apparently, steric effects and percentage of enol form in the starting β-dicarbonyl compound control the reaction rate and the nature of the observed products.

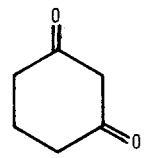
Table 1. Products, conditions and yields for the reaction of β-dicarbonyl compounds with TME.

β-dicarbonyl compound	Reaction product	Reaction time	Temperature	Solvent	Yield(%)[a]
Ia	Ib	72 h	100º	None	94.3
IIa	IIb	72 h	110º	None	51.0
IIIa	IIIb	22 h	120º	None	69.8
IVa	IVb	0.5h	110º	None	95[b]
Va	Vb[2]	1 h	100º	PhCl	74.2
VIa	VIb + VIc	115 h	130º	None	41 + 31[c]

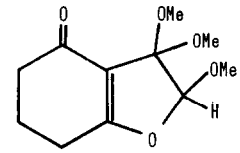
a) Yield of distilled product based on β-dicarbonyl compound. b) This product decomposes on distillation. The yield is calculated from the NMR spectrum of the crude product. c) The yield is calculated from the NMR spectrum of the distilled mixture.



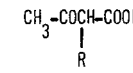
Ia, R = H
Ib, R = $-C(OMe)_2-CH(OMe)_2$



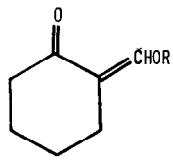
IIa



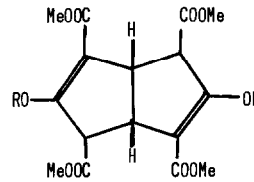
IIb



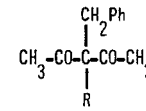
IIIa, R = H
IIIb, R = $-C(OMe)_2-CH(OMe)_2$



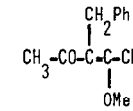
IVa, R = H
IVb, R = $-C(OMe)_2-CH(OMe)_2$



Va, R = H
Vb, R = Me



VIa, R = H
VIb, R = Me



VIc

SPECTROSCOPIC DATA

Compound	^{1}H NMR(CCl_4)(δ scale)	IR(solvent)	MS, 70eV, m/e(% rel. abun.)
Ethyl 1-(1,1,2,2-tetramethoxyethyl)-2-oxocyclopentanecarboxylate, Ib.	3.33(s,3H), 3.36(s,6H), 3.40(s,3H) diastereotopic $-C(\underline{OMe})_2-CH(\underline{OMe})_2$, 4.82(s,1H) $-\underline{CH}(OMe)_2$	(CCl_4) 1760 and 1730 cm^{-1}	289(0.9)(M^+-Me), 273(1.5), 259(1.3), 229(10.5), 149(6.8), 75(100).
2,3,3-Trimethoxy-2,3,4,5,6,7-hexahydrobenzo[b]furan-4-one, IIb.	3.42(s,3H), 3.48(s,3H), 3.56(s,3H), 4.25(s,1H) $-C(\underline{OMe})_2-\underline{CH}(OMe)-O-$	(CCl_4) 1675 and 1645 cm^{-1}	228(0.3)(M^+), 213(0.1), 198 (0.7), 197(1.1), 68(100).
Ethyl 2-(1,1,2,2-tetramethoxyethyl)-3-oxobutanoate, IIIb.	3.20(s,3H), 3.22(s,3H), 3.35(s,3H), 3.45(s,3H) $-C(\underline{OMe})_2-CH(\underline{OMe})_2$, 4.70(s,1H) $-\underline{CH}(OMe)_2$	($CHCl_3$) 1755, 1710 and 1655 cm^{-1}	263(0.05)(M^+-Me), 247(0.1), 233(0.04), 205(0.3), 149(1.9), 75(100).
2-(1,1,2,2-tetramethoxyethoxymethylen)cyclohexanone, IVb.	3.18(s,6H), 3.23(s,6H), 4.10(s,1H) $-O-C(\underline{OMe})_2-\underline{CH}(OMe)_2$, 7.48(t, J = 2Hz, 1H) $-\underline{CH}-O-$	(film) 1680 and 1600 cm^{-1}	243(2.1)(M^+-MeO), 199(3.0), 149(50.9), 75(100).

Satisfactory elemental analyses were obtained for compounds Ib, IIb, IIIb and Vb.

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2. S.P. Bathnagar, U. Weiss and R.J. Highet, J. Org. Chem. 42, 3089(1977).