Divergence of Carbonyl Ylide Reactions as a Function of Diazocarbonyl Compound and Aldehyde Substituent – Dioxolanes, Dioxolenes, and Epoxides

Albert E. Russell,[†] Jonathan Brekan,[‡] Luisa Gronenberg,[‡] and Michael P. Doyle^{*‡}

[†]*Department of Chemistry and Biochemistry, University of Maryland, College Park,
Maryland, 20742*

[‡] *Department of Chemistry, University of Arizona, Tuscon, Arizona 85721*

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General. ¹H NMR (250 MHz, 400 MHz, 500 MHz or 600 MHz) and ¹³C NMR (62.5 MHz, 100 MHz, 125 MHz or 150 MHz) spectra were obtained from solutions of CDCl₃. Chemical shifts are reported in ppm from tetramethylsilane (TMS). HRMS were obtained by HR-FAB method. Anhydrous THF was distilled from sodium/benzophenone ketyl. Dichloromethane was passed through a solvent column prior to use and was not distilled. The solvent columns are composed of activated alumina (A-2).¹ Dimethyl diazomalonate² and methyl diazoacetoacetate³ were prepared according to previously reported procedures. Methyl 3-*tert*-Butyldimethylsilanyloxy-2-diazobut-3-enoate was prepared according to a previously reported procedure.⁴

References

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- (3) Davies, H.M.L.; Cantrell, W.R., Jr.; Romines, K.R.; Baum, J.S. *Org. Syn.* **1991**, *70*, 93.
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Selective ID Transient NOE
using DPGSE for selection
Nalorac 3-res 3-axis gradient probe
2jb29.cis noe@6.14ppm

Selective 1D Transient NOE
using DPGSE for selection
Nalorac 3-res 3-axis gradient probe
2jb29.cis noe@5.96ppm

cis-10e

12b

12d

13c

13b124-3.f5-10.c13
Pulse Sequence: zgpg30

14a

13C NMR (CDCl₃)
Pulse Sequence: zgpg30

Table 1a. Divergence in Product Formation from Rh₂(OAc)₄-Catalyzed Reactions of Dimethyl Diazomalonate with Excess Aldehyde^a

Entry	Ar =	isolated yield, % ^b	10:11 ^c	<i>cis</i> - 10 : <i>trans</i> - 10 ^c
		10+11	2.0 eq(5.0 eq)	
		2.0 eq(5.0 eq)		
a	<i>p</i> -MeOC ₆ H ₄	20(--)	0:100(--)	--
b	<i>p</i> -MeC ₆ H ₄	17(14)	36:64(51:49)	1.5:1(1.5:1)
c	C ₆ H ₅	35(20)	75:25(91:9)	1.4:1(1.7:1)
d	<i>p</i> -ClC ₆ H ₄	28(4.0)	83:17(95:5)	1.7:1(1.7:1)
e	<i>p</i> -F ₃ CC ₆ H ₄	39(14)	100:0(100:0)	1.4:1(1.4:1)
f	<i>p</i> -NO ₂ C ₆ H ₄	6.0(--)	100:0(--)	1.9:1(--)

^aReactions performed in refluxing dichloromethane with 1.0 mol %Rh₂(OAc)₄ and 2.0 eq or 5.0 eq of aldehyde, based on diazomalonate.^bIsolated weight yield of chromatographically pure **10+11**. ^cDetermined by¹H NMR analyses prior to chromatographic purification.