# VACUUM FLASH PYROLYSIS (VFP) OF MALONYL PEROXIDES:
DECARBOXYLATION VERSUS DECARBONYLATION OF THE
INTERMEDIARY α-LACTONES

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SUMMARY: Vacuum Flash Pyrolysis (VFP) at ca. 450-500°C and ca. 0.1-0.3 Torr of the spirocyclic malonyl peroxides (2a,b) affords high yields of allenes (5a,b), while the simple malonyl peroxide (2c) leads to ketone (4), derived respectively from decarboxylation and decarbonylation of the intermediary α-lactones (3).

Previously we showed[2] that malonyl peroxides (2), conveniently prepared from the corresponding malonic acids (1) via methanesulfonic acid-catalyzed cyclization with concentrated hydrogen peroxide, produce α-lactones (3) on thermal or photochemical decarboxylation (eq.1). The fate of the reactive

(EQ.1)

(1)   (2)   (3)   (4)
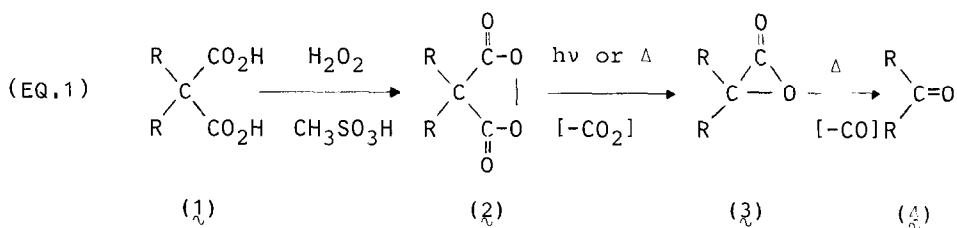
α-lactone intermediates (3) depends on the reaction conditions, e.g. polymerization to polyesters in the absence of nucleophiles, trapping in the form of

α-alkoxycarboxylic acids in the presence of alcohols as nucleophiles, or decarbonylation into ketones 4.[2] Apparently decarboxylation of (3) to give carbene-derived products is unfavorable. Thus, gas phase thermolysis at elevated temperatures of the spirocyclic trimethylenemalonyl peroxide gave cyclobutanone as major product and only small amounts of cyclobutene.[3]

In the spectroscopic detection of the α-lactones (3) through matrix isolation,[2c] we noted that the spirocyclic malonyl peroxide ($2a$) gave exclusively allene ($5a$), detected by IR, on photolysis (eq.2). Not even traces of

(EQ.2)
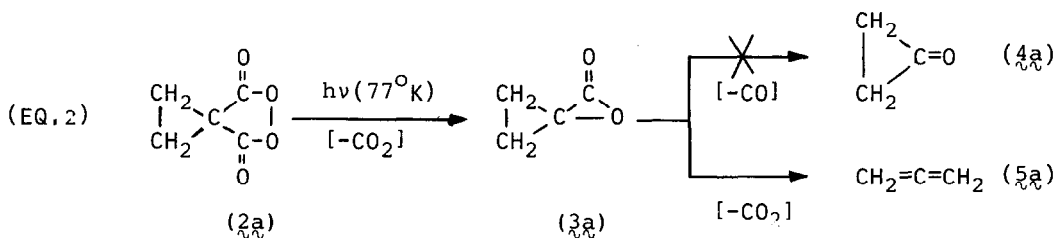
the expected cyclopropanone ($4a$) were formed. Presumably the highly strained ($3a$) prefers to decarboxylate into allene ($5a$), most likely via the cyclopropylidene as intermediate, than decarbonylate into the strained ($4a$).

In view of these results, we expected that under VFP conditions ($2a$) should produce allene ($5a$). Indeed, when a sample of solid ($2a$) was sublimed at 0.6 Torr through a hot (ca. 450°C) quartz tube and the gaseous products condensed in a liquid nitrogen cooled trap, allene ($5a$) was formed in ca. 50% yield, detected by IR (1951 cm^{-1}). However, the di-n-butylmalonyl peroxide ($2c$) gave under these VFP conditions a ca. 70% yield of 5-nonanone ($4c$), i. e. the decarbonylation product of the intermediary α-lactone ($3c$). Only traces ($\leq 2\%$) of 4-nonene, the decarboxylation product of ($3c$), could be detected. Consequently, spiro-annelation is a necessary requisite for the decarboxylation of α-lactones into allenes.

This novel and synthetically valuable route to allenes was further exploited in the synthesis of 1,2-cyclononadiene ($5b$). The hitherto unknown spirocyclic malonyl peroxide ($2b$) was prepared from the corresponding malonic acid ($1b$) in 51% yield.[4] On VFT (ca. 450°C and 0.16 Torr) the cyclic allene ($5b$) was

formed in ca. 50% yield (eq.3). It is significant to mention that when the

(eq.3)   (2b)   VFP →   (5b)   (6)
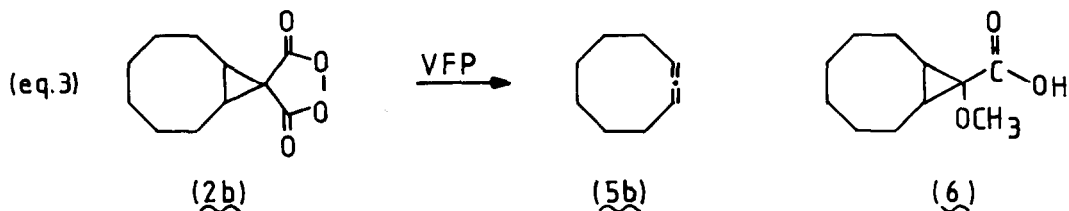
pressure of the VFP was ca. 10 mm, only polyester was formed in the reaction
vessel. Under these relatively high pressures (2b) was apparently not suffi-
ciently volatile to be sublimed through the hot quartz tube and the α-lactone
(3b) that was formed in the reaction vessel was destined to polymerize. Fur-
thermore, on photolysis in benzene solution at 350 nm also only polyester was
formed. When the 350 nm photolysis was performed in methanol as solvent, the
α-alkoxycarboxylic acid (6) was formed in ca. 95% yield.[5] Consequently, only
under the VFP conditions do the spirocyclic malonyl peroxides produce allenes.
We are in the process of exploring the general scope of this potentially use-
ful synthetic method for allenes.

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1. NIH Career Awardee (1975-80); direct correspondence to the Würzburg address.

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c) Chapman, O. L.; Wojtkowski, P. W.; Adam, W.; Rodriguez, O.; Rucktäschel, R. *J. Am. Chem. Soc.* 1972, *95*, 1365. For additional characterization of malonyl peroxide (2a), we report its ^{13}C NMR (CDCl$_3$) δ (ppm) 19.74, 23.58, 172.08. Furthermore, the ^{1}H NMR shows a large solvent effect, i.e. in CCl$_4$ δ 1.97 ppm (sharp singlet) and in C$_6$D$_6$ δ 0.93 ppm (sharp singlet).

d) Adam, W.; Rucktäschel, R. 1971, *93*, 557.

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4. (2b); mp 104°C (needless from pentane); correct elemental composition for the C$_{11}$H$_{16}$O$_4$ empirical formula by combustion analysis; ^{1}H-NMR (CDCl$_3$) δ (ppm) 1.57 (br.s, 8H), 1.9 (m, 4H), 2.44 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ (ppm) 19.83, 26.00, 27.79, 43.94, 221.36; IR (CHCl$_3$) ν (cm^{-1}) 3030, 2940, 2860, 1811, 1786, 1320, 1195.

5. (6); liquid; ^{1}H-NMR (Cll$_4$) δ (ppm) 1.50 (br.s, 14H) 3.16 and 3.26 (s, 3H), 9.03 (s, 1H;exchange with D$_2$O); ^{13}C-NMR (CDCl$_3$) δ (ppm) 20.96, 26.16, 26.17, 28.65, 33.91, 49.90, 55.85, 56.16, 66.14, 176.77, 221.68; IR (CCl$_4$) ν (cm^{-1}) 3550, 2945, 2860, 2710, 2600, 1695, 1450, 1320, 1200. Both isomers are formed in ca. 1:1 ratio; stereochemistry undefined.