

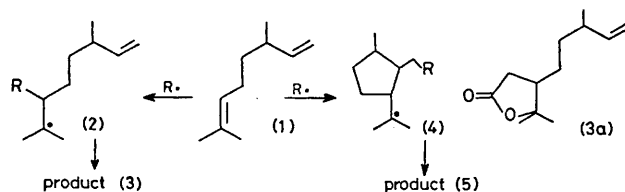
Selectivity in the Addition of Organic Radicals to the Alkene Bond

By JOHN H. EDWARDS, FRANCIS J. McQUILLIN,* and MICHAEL WOOD

(Department of Organic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU)

Summary The selective addition of difunctional radical addends, *e.g.* $R_2\dot{C}-O$, $R = Me$ or Ph , to the 6,7-alkene centre of 3,7-dimethylocta-1,6-diene, and of monofunctional radicals, *e.g.* $Me_2\dot{C}OH$, 1,3-dioxolanyl, and tetrahydrofuryl radicals at the 1,2-bond is rationalised.

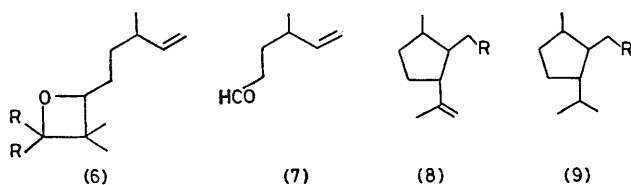
In addition reactions to the diene (1), organic radicals, generated by Mn^{III} triacetate oxidation: $RH + Mn^{III} \rightarrow R\cdot + Mn^{II} + H^+$, react by pathways¹ (1) \rightarrow (5) or (1) \rightarrow (3) depending on the nature of the substituents in the addend radical. Radicals such as $\cdot CH_2CO_2H$ or $\cdot CH(COMe)_2$, capable of product formation by oxidative cyclisation react principally by pathway (1) \rightarrow (3), *e.g.* $\cdot CH_2CO_2H \rightarrow$ (3a), whereas chemically monofunctional radicals such as $\cdot CH_2COR$ or $\cdot CH(CO_2Me)_2$ yield exclusively products of type (5).



These interesting observations led us to extend our study to include photochemically generated radicals.

The diene (1), when irradiated (Hg lamp) in the presence of acetone (with cooling) gave in 20% yield a product (6, $R = Me$), showing an $M - 15$ ion at m/e 181, and a significant fragment ion at m/e 138 ($M - 58$; $Me_2C=O$), and in the n.m.r. spectrum the characteristic vinyl proton pattern δ 4.8–6.1 (3H), together with a 1H triplet at δ 4.17, a 3H

doublet at 1.0, and singlets at 1.07 (6H), 1.66 (3H), and 1.29 (3H). Benzophenone similarly gave (**6**, R = Ph), 80%, $M - 1$ ion at m/e 319, and m/e 208 ($\text{Ph}_2\text{C}=\text{CMe}_2$) and 182 (Ph_2CO), δ 4.8–6.1 (3H, vinyl), 4.3 (1H, t), 1.03 (9H, m), and 7.4 (10H, m). A product (**6**, RR = Ph, H) was obtained in the same way from (**1**) and benzaldehyde.



Thus the ketone triplets add selectively to the 6,7-bond with cyclisation. Incidentally, (**6**, R = Ph) is a useful source of (**7**) by acid-induced fragmentation ($p\text{-MeC}_6\text{H}_4\text{-SO}_3\text{H}$ in ether, reflux 1 h).

By contrast, (**1**), with tetrahydrofuran and acetone as sensitiser,² gave (**8**, R = 2-tetrahydrofuryl) as the minor, and [**8**, R = C(OH)Me₂] as the major product. The former was characterised by $M = 208.1826$ ($\text{C}_{14}\text{H}_{24}\text{O}$), δ 0.94 (3H, br.s), 1.8–2.2 (4H, m), 1.1–1.6 (9H, m), 1.67, (3H, s), 3.6 (3H, m), and 4.74 (2H, br s). The major product, ν 3350 cm^{-1} , gave m/e 196 ($\text{C}_{13}\text{H}_{24}\text{O}$), δ 0.91 (3H, d), 1.19 (6H, s), 1.7 (3H, s), and 4.97 (2H, br s).

The 1,3-dioxolanyl radical, generated in the same way, gave (**8**, R = 2- and 4-dioxolanyl), $M = 210.1616$ ($\text{C}_{13}\text{H}_{22}\text{O}_2$), δ 0.9 (3H, d), 1.7 (3H, s), 3.79 (4H, m), and 4.74 (3H, =CH₂ and -O-CH-O). This material was accompanied by the expected² products of further photolysis (**9**, R = CO₂-Et), ν 1720 cm^{-1} , $M = 212.1788$, δ 0.94 (9H, br), 4.05 (2H, q), and 1.3 (3H, t), and (**9**, R = CH₂CH₂OCHO), ν 1725 cm^{-1} , $M = 212.1769$, δ 0.94 (9H, br), 4.1 (2H, m), and 8.08 (1H, s). However, [**8**, R = C(OH)Me₂] was not

isolated and there are thus indications of an order of reactivity: 2-dioxolanyl > 1-hydroxy-1-methylethyl > tetrahydrofuryl. We note from the structure of products (**9**) evidence for internal H-transfer from the dioxolanyl to the -CMe₂ residue.

The significant result is, however, the preferential addition of these mono radicals to the 1,2-alkene of (**1**), so that the results of photo-induced addition replicate those obtained with radicals generated oxidatively. The accumulated results may be summarised as in the Table.

TABLE

Radicals giving product (3)	Radicals giving product (5)
$\cdot\text{CH}_2\text{CO}_2\text{H}^{\text{a},\text{b}}$	$\cdot\text{CH}_2\text{COR}^{\text{b},\text{c}}$
$\cdot\text{CH}(\text{COMe})_2^{\text{a},\text{b}}$	$\cdot\text{CH}(\text{CO}_2\text{Me})_2^{\text{b}}$
$\cdot(\text{CH}(\text{COMe})\text{CO}_2\text{Et})^{\text{b}}$	2-Oxocyclopentyl ^b
$\text{R}_2\dot{\text{C}}-\dot{\text{O}}^{\text{c}}$	2-Oxocyclohexyl ^b
$\text{Ph}\dot{\text{C}}\text{H}-\dot{\text{C}}$	$\cdot\text{C}(\text{OH})\text{Me}_2$
	Tetrahydro-2-furyl
	1,3-Dioxolan-2-yl

^a (**5**) also obtained as a minor product. ^b Ref. 1. ^c R = Ph or Me.

In explanation we have considered¹ reversible addition of monofunctional radicals at the 6,7-alkene bond, *i.e.* making (**3**) the kinetic and (**5**) the thermodynamic products. However, frontier orbital control could offer an alternative rationalisation of our results. The 6,7- and 1,2-bonds of (**1**) should have HOMO levels³ lying at 8.8 and 9.7 eV, respectively, and the triplet ketones⁴ and radicals⁵ $\cdot\text{CH}_2\text{-COR}$ and $\cdot\text{CH}(\text{CO}_2\text{Me})_2$ SOMO levels at *ca.* 6.5 eV and > 9.8 eV, respectively, *i.e.* in agreement with their modes of reaction. For $\cdot\text{CH}_2\text{CO}_2\text{H}$,⁶ I.P. *ca.* 10.9 eV, or $\text{Me}_2\dot{\text{C}}\text{OH}$,⁷ I.P. < 7 eV, however, the observed selectivity does not sustain frontier orbital control.

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⁷ Based on MeCHOH, ref. 3.