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THE REACTION OF t-BUTOXYL RADICALS WITH GLYCIDOLS AND THEIR *O*-TRIBUTYLTIN DERIVATIVES: HOMOLYTIC 1,5-TRANSFER OF HYDROGEN AND OF TIN FROM ENOXYL OXYGEN TO ALKOXYL OXYGEN

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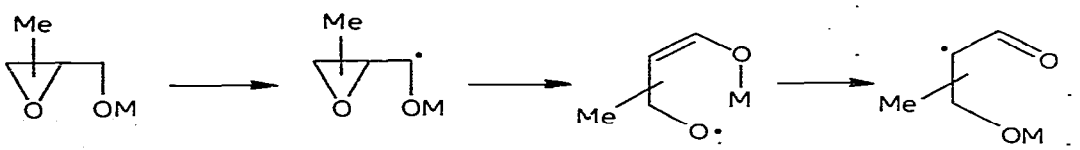
Summary

The interaction of t-butoxyl radicals with glycidol, α-, β-, and γ-methylglycidol, and their *O*-tributyltin derivatives (A, M = H or Bu_3Sn) have been studied by ESR spectroscopy.

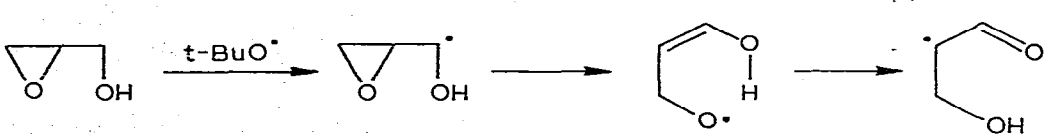


(A) (B) (C) (D)

The radicals B and C are formed successively. In C, the tributyltin group, or the hydrogen atom, then undergoes an intramolecular 1,5- rearrangement from enoxyl oxygen to alkoxyl oxygen, and the spectra of the enoxyl radicals D are observed.

Introduction

We recently reported briefly the results of an ESR study of the reaction of t-butoxyl radicals with glycidol (I) [1].



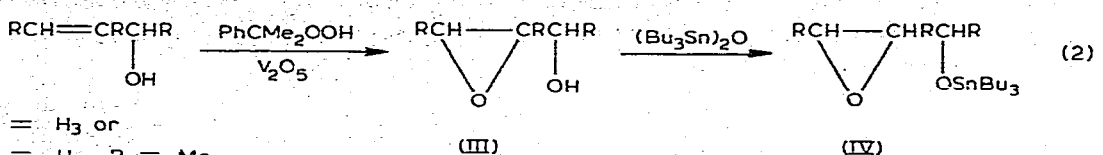
(I) (II) (1)

The principal spectrum which was observed was that of the enoxyl radical (II) which was thought to be formed by ring-opening of the first-formed exocyclic radical, followed by an intramolecular 1,5-transfer of hydrogen from the enoxyl oxygen to the alkoxyl radical; this type of intramolecular transfer of hydrogen, but from enolic oxygen to carbon, had been established much more thoroughly with the corresponding homocyclic compounds, the cyclopropylcarbinols [1,2]. The reaction of glycidol showed also a doublet spectrum resulting from a second species (a 19.5 G) which at that time was not identified, but from its low g-value (ca. 2.0008), appeared to be a σ-radical.

We now report a study of the reaction of t-butoxyl radicals with glycidol, α-, β-, and γ-methylglycidols, and their *O*-tributyltin derivatives. All the protic compounds show the same 1,5-hydrogen transfer reactions as glycidol itself, while the tin compounds provide the first examples of the analogous intramolecular transfer of an organometallic group.

Discussion

The α-, β-, and γ-methyl glycidols (III) were prepared by epoxidation of the corresponding methylallyl alcohols with cumene hydroperoxide in the presence of vanadium pentoxide, and were converted into the *O*-tributyltin derivatives (IV) by azeotropic dehydration in the presence of bis(tributyltin) oxide.



Di-t-butyl peroxide was then photolysed in the presence of the glycidols and their tributyltin derivatives in cyclopropane solution, and the radicals which were formed were monitored by ESR spectroscopy. The results are summarised in Table 1. Some related radicals derived from the corresponding cyclopropyl carbinols are included for comparison as footnotes.

Apart from the doublet in the spectrum from glycidol referred to above, all the reactants showed the spectrum of a single radical species. The consistent high g-values (ca. 2.0045) are characteristic of enoxyl radicals, and the low doublet couplings (ca. 18 G) of the structure —CH—CR=O. The splitting patterns conform with those predicted for the radicals HOCHRĊRCR=O or $Bu_3SnOCHR\dot{C}RCR$=O, derived from the reactants III or IV respectively, and the identity of the radical $HOCH_2\dot{C}HCH$=O was established by preparing it from an independent route [1]. We conclude that the methylglycidols undergo the same type of ring-opening and hydrogen-transfer as glycidol itself (cf. eq. 1), and that the tributyltin compounds take part in a similar reaction which involves the intramolecular 1,5-transfer of the tributylstannyl group from enoxyl oxygen * to alkoxy oxygen

* *O*-Stannyl enolates, in metallotropic equilibrium with their *C*-stannyl isomers, can be prepared inter alia from the reaction of enol acetates with tin alkoxides [3]. No investigation of their homolytic reactivity appears to have been reported.

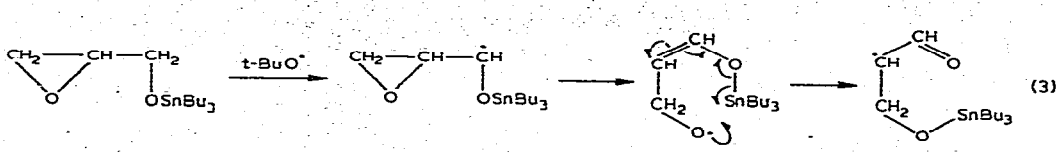
TABLE 1

RADICALS OBSERVED IN THE PHOTOLYSIS OF DI-t-BUTYL PEROXIDE IN THE PRESENCE OF GLYCIDOLS AND *O*-TRIBUTYLTIN GLYCIDOLS IN CYCLOPROPANE

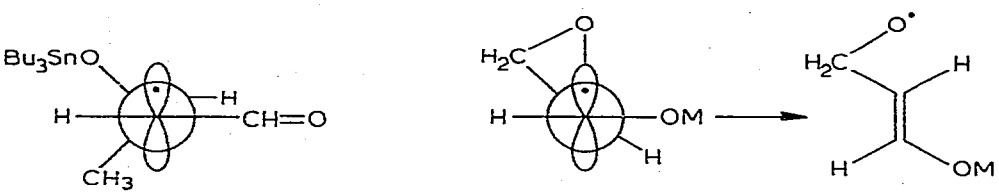
Reactant	Product	Hyperfine coupling constants				
		$a(H\alpha)$ (G) [d]	$a(H\beta)$ (G) [d]	$a(H)$ (G) [d]	g	T (°C)
$\overline{OCH_2}\dot{C}HCH_2OH$	$HOCH_2\dot{C}HCH{=}O$ [a]	18.3(1)	27.3(2)	1.2(1)	2.0045	−30
$\overline{OCH_2}\dot{C}HCH_2OSnBu_3$	$Bu_3SnOCH_2\dot{C}HCH{=}O$	18.0(1)	26.4(2)	1.1(1)		−40
$\overline{OCH_2}\dot{C}HCH(CH_3)OH$	$HOCH_2\dot{C}HC(CH_3){=}O$ [b]	18.3(1)	28.0(2)	1.1(3)	2.0046	−30
$\overline{OCH_2}\dot{C}HCH(CH_3)OSnBu_3$	$Bu_3SnOCH_2\dot{C}HC(CH_3){=}O$	18.5(1)	27.0(2)	1.0(3)	2.0044	−80
$\overline{OCH_2}\dot{C}(CH_3)CH_2OH$	$HOCH_2\dot{C}(CH_3)CH{=}O$		21.0(5) [e]	2.1(1)	2.0041	−70
$\overline{OCH_2}\dot{C}(CH_3)CH_2OSnBu_3$	$Bu_3SnOCH_2\dot{C}(CH_3)CH{=}O$		21.2(5) [f]	1.9(1)	2.0046	−80
$\overline{OCH(CH_3)}\dot{C}HCH_2OH$	$HOCH(CH_3)\dot{C}HCH{=}O$ [c]	18.0(1)	15.0(1)	1.1(4)	2.0046	−20
				3.0(3)		
$\overline{OCH(CH_3)}\dot{C}HCH_2OSnBu_3$	$Bu_3SnOCH(CH_3)\dot{C}HCH{=}O$	17.5(1)	8.8(1)	1.4(1)	2.0046	−80

[a] cf. ref. 1. $CH_3CH_2\dot{C}HCH{=}O$: $a(H\alpha) = 18.4$, $a(2H\beta) = 19.8$, $a(CHO) = 0.8$ G at +16°C. [b] cf. ref. 1. $CH_3CH_2\dot{C}HC(CH_3){=}O$; $a(H\alpha) = 18.9$, $a(2H\beta) = 20.8$, $a(CH_3) = 1.0$ G at −34°C. [c] cf. ref. 1. $(CH_3)_2CH\dot{C}H(CH_3)O$: $a(H\alpha) = 18.7$, $a(H\beta) = 9.5$, $a(6H\gamma) = 0.8$ G at −16°C. [d] The number of coupling hydrogens are given in parentheses. [e] Above −70°C, further lines can be detected of a similar spectrum with the same g-value and coupling constants of 2.0 and 22.5 G, but with an overall span about 8.5 G less. This may be associated with rotational isomerism about the CH_2—OH and CH—CHO bonds. [f] $a(CH_2)$ decreases above −70°C.

(e.g. eq. 3). On the other hand, only hydrogen and not the tributylstannyl group can be transferred from enoxyl oxygen to carbon in the corresponding ring-opening reactions of cyclopropylcarbinols and their tributyltin derivatives [4].



The hyperfine coupling constants of the β-CH_2 group in the radicals $HOCH_2$-$\dot{C}HCR{=}O$ and $Bu_3SnOCH_2\dot{C}HCR{=}O$ are larger than those in the corresponding radicals $CH_3CH_2\dot{C}HCR{=}O$ derived from the cyclopropylcarbinols (see footnotes to Table 1), implying that the hydroxy and stannyloxy groups have a larger tendency than the methyl group to lie in the modal plane of the *p*-orbital containing the unpaired electron. The pair of radicals $HOCH(CH_3)\dot{C}HCH{=}O$ and Bu_3SnOCH-$(CH_3)\dot{C}HCH{=}O$ were exceptional in that whereas both showed a small value of $a(H\beta)$, that for the stannyloxy-substituted radical was much the smaller. This is reasonable as the bulky methyl and tributylstannyloxy substituents on the β-carbon atom would tend to be oriented in the gauche positions away from the CHO group, causing the hydrogen on the β-carbon to lie in a time-averaged position near the nodal plane of the *p*-orbital containing the unpaired electron as in V. A similar situation exists in the radical $Me_2CH\dot{C}HMe{=}O$ (Table 1, footnote *c*).



(V) (VI) (VII)

The ESR spectra show that ring-opening by cleavage of the C—C rather than the C—O bond is not a significant reaction even when the γ-carbon carries a methyl group and C—C cleavage would give a secondary alkyl radical. On the other hand they cannot exclude the possibility that some ring opening might occur through the conformer VI to give the *trans*-enolate (VII, M = H or Bu_3Sn) which presumably could not undergo a 1,5-rearrangement. This may be relevant to the unidentified doublet which was observed with glycidol itself. We hope to return to the identity of this doublet in a subsequent publication.

Experimental

Samples for ESR spectroscopy were sealed in cyclopropane solvent in Suprasil silica tubes. Spectra were recorded on a Varian E4 instrument fitted with a high pressure mercury discharge lamp for photolysis within the cavity [1,4] and with provision for the accurate measurement of the magnetic field and microwave frequency.

Preparation of glycidols

Glycidol was a commercial sample (Emanuel) and was distilled before use.

The methylglycidols were prepared by epoxidation of the appropriate α-, β-, or γ-methylallyl alcohol (Aldrich) using cumene hydroperoxide in the presence of vanadium pentoxide as catalyst [5]. The following procedure is typical.

A mixture of 2-methylallyl alcohol (15.0 g, 0.21 mol), cumene hydroperoxide (15.8 g, 0.12 mol), and vanadium pentoxide (0.18 g, 0.01 mol) was heated at 60°C, under reflux, for 7 h. The catalyst was filtered off, the crude β-methylglycidol was isolated by distillation, then carefully redistilled to remove residual cumyl alcohol. Yields were usually about 30% (based on hydroperoxide). List and Kuhnen [5] report 78—80%.

The characteristics of the products were as follows: 2-(1-Hydroxyethyl)-oxiran, b.p. 70°C at 28 mmHg, τ (in CCl_4) 6.0—6.6 (m, C<u>H</u>OH), 6.93 (b, OH), 7.0—7.4 (m, ring CH_2CH), 8.80 (d, CH_3 J 7 Hz); 2-Hydroxymethyl-2-methyl-oxiran, b.p. 89°C at 28 mmHg, τ (in CCl_4) 6.44 (b, OH), 6.44 (s, C<u>H</u>$_2$OH), 7.21 (d, ring C<u>H</u>^{A}H^B), 7.47 (d, ring CH^A<u>H</u>^{B}, J(H^{A}H^B) 5 Hz), 8.70 (s, CH_3); 2-Hydroxy-methyl-3-methyloxiran, b.p. 75°C at 28 mmHg, τ (in CCl_4) 6.10 (b, OH), 6.37 (b, CH_2) 6.90—7.35 (m, ring CHCH), 8.72 (d, CH_3 J 5 Hz). The oxiran probably has the *trans*-structure, as the IR spectrum of the γ-methylallyl alcohol corresponded with that of the *trans*-compound [6] and the oxidation probably involves *cis*-addition [7].

Preparation of O-trialkyltin derivatives

The *O*-trialkyltin derivatives of the glycidols were prepared by azeotropic dehydration of a mixture of the glycidol and bis(tributyltin) oxide using a Dean and Stark water separator, following a general procedure [8]. The products showed the following properties.

2-(Tributylstannyloxymethyl)oxiran, b.p. 120°C at 0.2 mmHg, τ (in CCl_4) 6.06 (m, CH^{A}C<u>H</u>^{B}H^{C}OSn), 6.43 (m, CH^{A}CH^B<u>H</u>^{C}OSn, J(H^{A}H^B) 3 Hz, J(H^{A}H^C) 4 Hz, J(H^{B}H^C) 12 Hz), 6.98—7.23 (m, ring CH), 7.34—7.56 (m, ring CH_2), 8.20—9.40 (b, Bu_3Sn). Analysis: Found: C, 50.0; H, 8.99. $C_{15}H_{32}O_2Sn$ calcd.: C, 49.6; H, 8.88%.

2-(1-Tributylstannyloxyethyl)oxiran, b.p. 85°C at 0.05 mmHg, τ (in CCl_4), 6.00—6.37 (C<u>H</u>OSn), 7.1—7.69 (m, ring CH_2CH), 8.2—9.24 (b, Bu_3Sn), 8.90 (d, CH_3, J 7 Hz). Found: C, 50.9; H, 9.07. $C_{16}H_{34}O_2Sn$ requires C, 51.0; H, 9.08%.

2-(Tributylstannyloxymethyl)-2-methyloxiran, b.p. 95°C at 0.05 mmHg, τ (in CCl_4) 6.36 (s, CH_2OSn), 7.33 (d, ring C<u>H</u>^{A}H^B), 7.60 (d, ring CH^A<u>H</u>^{B}, J 6 Hz), 8.16—9.28 (b, Bu_3Sn); 9.75 (s, CH_3). Analysis: Found: C, 51.2; H, 9.06. $C_{16}H_{34}O_2Sn$ calcd.: C, 51.0; H, 9.08%.

2-(Tributylstannyloxymethyl)-3-methyloxiran, b.p. 104°C at 0.05 mmHg. τ (in CCl_4) 6.13 (d, CH^A<u>H</u>^{B}H^{C}OSn, J(H^{A}H^B) 4 Hz), 6.40 (d, CH^{A}CH^B<u>H</u>^{C}OSn, J(H^{A}H^C) 5 Hz, J(H^{B}H^C) 12 Hz), 7.0—7.5 (m, ring, CHCH), 8.75 (d, CH_3 J 5 Hz), 8.20—9.50 (b, Bu_3Sn). Analysis: Found: C, 50.1; H, 9.00. $C_{16}H_{34}O_2Sn$ calcd.: C, 51.0; H, 9.08%).

Acknowledgements

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