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# STEREOCHEMISTRY OF THE 2,4-DIMETHYL-1,3-DIOXOLAN-2-YL RADICAL

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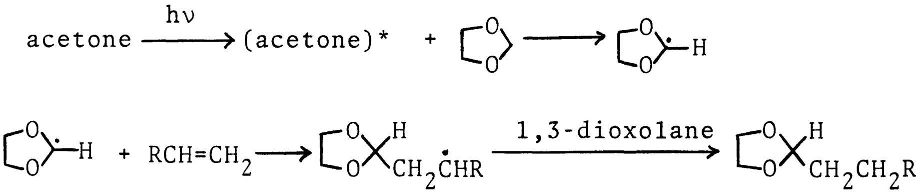
The acetone-initiated photochemical addition of cis- or trans-2,4-dimethyl-1,3-dioxolane to methyl acrylate at -78°C leads to a mixture of geometrically isomeric methyl 3-(2,4-dimethyl-1,3-dioxolan-2-yl)propionates with partial retention of the original configuration of the starting dioxolane. This constitutes evidence for a pyramidal structure of the radical centre of 1,3-dioxolan-2-yl radicals involved as an intermediate in the photochemical addition.

The geometry at the tervalent carbon atom of 1,3-dioxolan-2-yl radicals has been studied by examining the esr hyperfine coupling,1) but the theme has not been approached through investigating reactions undergone by such radicals. We now present chemical evidence for a pyramidal configuration of the tervalent carbon atom of the 2,4-dimethyl-1,3-dioxolan-2-yl radical.

The acetone-initiated photochemical addition of 1,3-dioxolane to olefins is known to be a radical chain reaction:2)

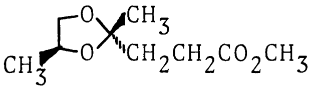
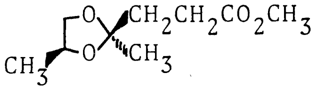
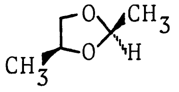
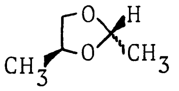


The corresponding reactions of 2,4-dimethyl-1,3-dioxolane with methyl acrylate, diethyl maleate and 1-hexene have been found to give 1:1 adducts in yields of 4, 78 and 26%, respectively.

cis- and trans-2,4-Dimethyl-1,3-dioxolane ($I_c$ and $I_t$) were prepared by reaction of propylene glycol with acetaldehyde in the presence of p-toluenesulphonic acid and anhydrous magnesium sulphate[3)] and by gas chromatographic separation (with a 4.5 m x 8 mm stainless steel column packed with polyethylene glycol succinate at 94°C) of the reaction product. The geometrical configurations were assigned by comparison of their nmr spectra in carbon tetrachloride.[4)] A mixture of cis- or trans-2,4-dimethyl-1,3-dioxolane ($I_c$ or $I_t$) (2.0 ml), acetone (0.25 ml) and methyl acrylate was irradiated with a 100-watt high-pressure mercury lamp for 2 hours and the product (a mixture of methyl 3-(2,4-dimethyl-1,3-dioxolan-2-yl)propionates, $IV_c$ and $IV_t$) was analyzed for the isomeric composition by gas chromatography with a polyethylene glycol succinate column at 100°C. The results are given in Table 1.

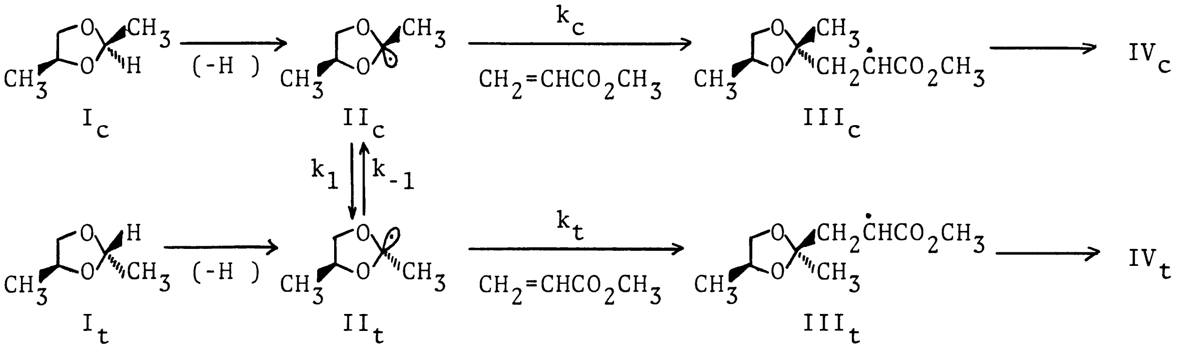
Table 1

Results of Acetone-initiated Photochemical Addition of Methyl Acrylate to cis- and trans-2,4-Dimethyl-1,3-dioxolane

| Dioxolane | Methyl acrylate | Temp. | Product isomer ratio* | |
|---|---|---|---|---|
| | | |  |  |
| | mole/l | °C | IVc % | IVt % |
| <br>$I_c$ | 0.493 | room temp. | 60.5 | 39.5 |
| | 0.0987 | -78 | 73.5 | 26.5 |
| | 0.296 | -78 | 77.6 | 22.4 |
| | 0.395 | -78 | 80.1 | 19.9 |
| | 0.493 | -78 | 81.9 | 18.1 |
| <br>$I_t$ | 0.493 | room temp. | 62.5 | 37.5 |
| | 0.0987 | -78 | 43.4 | 56.6 |
| | 0.197 | -78 | 38.4 | 61.6 |
| | 0.296 | -78 | 36.7 | 63.3 |
| | 0.395 | -78 | 28.2 | 71.8 |

*Mean of duplicate runs

At room temperature, $I_c$ or $I_t$ yielded mixtures of $IV_c$ and $IV_t$ in approximately equal ratios, whereas, at -78°C, the products were richer in the isomer which retained the configuration of the starting dioxolane. The degree of the retention of configuration increased with the concentration of methyl acrylate. These findings are readily accommodated in a reaction sequence shown in Scheme 1, in which an inverting pyramidal structure is postulated for the 2,4-dimethyl-1,3-dioxolan-2-yl radical centre ($II_c$ and $II_t$). At room temperature, the interconversion between $II_c$ and $II_t$ is so fast that the equilibration has been completed before the radicals add to methyl acrylate, resulting in a product consisting of the isomeric adducts in the same ratio regardless of the configurating of the starting dioxolane, while at -78°C the interconversion is slow enough for methyl acrylate to be able to trap the dioxolanyl radical predominantly in the configuration corresponding to the starting dioxolane.



Scheme I

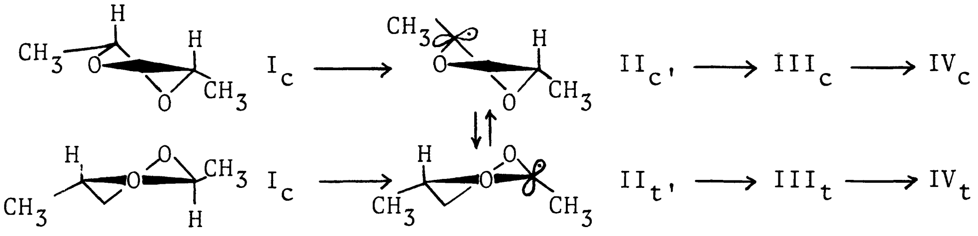
By reference to Scheme I and using the usual steady state approximation, the product isomer ratio $IV_c/IV_t$ is correlated with the concentration of the acrylate by the following equations:

for reactant $I_c$
$$\frac{IV_c}{IV_t} = \frac{k_c}{k_1}(\text{Methyl acrylate}) + \frac{k_c}{k_t}\cdot\frac{k_{-1}}{k_1}$$

and for reactant $I_t$
$$\frac{IV_t}{IV_c} = \frac{k_t}{k_{-1}}(\text{Methyl acrylate}) + \frac{k_t}{k_c}\cdot\frac{k_1}{k_{-1}}$$

As is expected from these equations, the plots of the isomer ratios at -78°C against the concentration of methyl acrylate represent straight lines, the slopes of which give $k_c/k_1 = 4.4 \pm 0.6$ and $k_t/k_{-1} = 3.9 \pm 0.7(\text{l}\cdot\text{mol}^{-1})$.

The possibility that 2,4-dimethyl-1,3-dioxolan-2-yl radical might have lost the configurational identity of the starting dioxolane, the radical being planar or, what amounts to the same thing in respect of the chemical reaction, inverting its pyramidal structure very quickly, and yet might retain the conformation of the parent compound (as, for example, $II_c{}'$ and $II_t{}'$ shown in Scheme II) may be excluded, because, with such a geometry, $II_c{}'$ or $II_t{}'$ would add to methyl acrylate on either side of the radical centre with comparable chances,[5] and it is very hard to envisage the way in which the addition takes place stereoselectively to yield $III_c$ or $III_t$.



Scheme II

Thus, the present results firmly establish the pyramidal nature of the 1,3-dioxolan-2-yl radical centre.

The diastereomeric structures of methyl 3-(2,4-dimethyl-1,3-dioxolan-2-yl)-propionates were determined by examining the psuedocontact paramagnetic shift of proton magnetic resonance of the alcohols derived from these esters by reduction with lithium aluminium hydride. The shifts, in carbon tetrachloride, induced by tris(dipivalomethanato)europium, Eu(DPM)$_3$, varied linearly with the molar ratios of Eu(DPM)$_3$ to the alcohols and the gradients (shift parameter)$^{6)}$ were evaluated. The shift parameters for the signals from the methyl groups (originally $\delta$ 1.26 or 1.21) at position 2 were nearly the same, being 3.91 or 4.01, respectively, but those for the methyls (originally $\delta$ 1.22 or 1.22) at position 4 were different, being 1.50 or 2.35. Thus, the alcohol that shows the larger induced shift and consequently the corresponding ester are assigned the structure in which the two methyl groups are situated trans to each other, i.e., structure IV$_t$ for the ester, and the other ester, accordingly, has the structure IV$_c$. Experiments with tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)praseodymium, Pr(FOD)$_3$, as a shift reagent led to the same conclusion.

All new compounds gave the required spectral and anlytical data.

## References

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