Oxidation of Olefins with Thallium(III) Acetate in Diols[1)]

Sakae Uemura,* Haruo Miyoshi, Akio Toshimitsu, and Masaya Okano

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

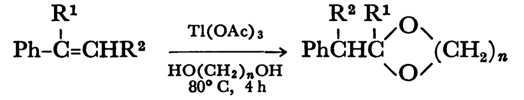
(Received May 19, 1976)

The oxidation of styrene, α- and β-methylstyrene, and 1-octene with thallium(III) acetate in diols, $\mathrm{HO(CH_2)_nOH}$ (n=2, 3, and 4), has been investigated. From styrene the derivatives of 1,3-dioxolane, 1,3-dioxane, and 1,3-dioxepane were mainly obtained for n=2, 3, and 4 respectively, while the reaction of 1-octene in 1,2-ethanediol afforded 1-acetoxy-2-(2-hydroxyethoxy)octane as the main product. A new alkoxythallate of styrene, $\mathrm{C_6H_5CH(OCH_2CH_2OH)CH_2Tl(OAc)_2}$, has been isolated under milder conditions.

Extensive data are available on the oxidation of olefins with metal salts in alcohols. However, there are only a few reports[2)] on the reaction with the use of a diol as an alcohol component. As an extension of studies on the alkoxythallation of olefins[3)] we now report the first example of the oxidation of olefins with thallium(III) acetate in various diols, $\mathrm{HO(CH_2)_nOH}$ (n=2, 3, and 4), where an intramolecular substitution of thallium moiety by hydroxy oxygen may be expected in the intermediate ω-hydroxyalkoxythallate of olefins. Isolation of a new alkoxythallate of styrene and its reactions are also reported.

Results and Discussion

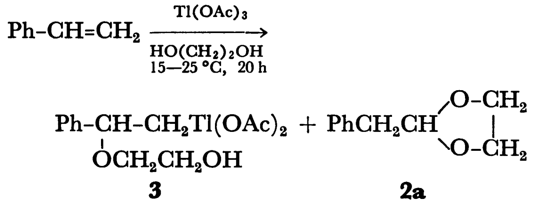
Reaction of styrene (**1a**) with thallium(III) acetate in 1,2-ethanediol, 1,3-propanediol, and 1,4-butanediol at 80 °C for 4 h gave 2-benzyl-1,3-dioxolane (**2a**, 36% yield), 2-benzyl-1,3-dioxane (**2d**, 33% yield), and 2-benzyl-1,3-dioxepane (**2e**, 17% yield) respectively, together with small amounts of phenylacetaldehyde and acetophenone in each case. Similarly, 2-methyl-2-benzyl-1,3-dioxolane (**2b**, 81% yield) and 2-(α-methylbenzyl)-1,3-dioxolane (**2c**, 23% yield) were formed from α- (**1b**) and β-methylstyrene (**1c**) respectively, by the use of 1,2-ethanediol as solvent. The ring products clearly arise from phenyl migration (Scheme 1). When the reaction of styrene with thallium(III) acetate in 1,2-ethanediol was carried out at room temperature, a new organothallium(III) compound (**3**) was isolated together with **2a** (Scheme 2). In order to ascertain **3** to be the intermediate for **2a**, the isolated **3** was heated in 1,2-ethanediol at 80 °C for 4 h. As expected, **2a** was obtained as the sole product.



$$\mathrm{Ph\text{-}\overset{R^1}{\overset{|}{C}}{=}CHR^2} \xrightarrow[\mathrm{HO(CH_2)_nOH},\ 80\,°\mathrm{C},\ 4\,\mathrm{h}]{\mathrm{Tl(OAc)_3}} \mathrm{PhCH\overset{R^2}{}\overset{R^1}{\overset{|}{C}}\genfrac{}{}{0pt}{}{\diagup O \diagdown}{\diagdown O \diagup}(CH_2)_n} \quad (1)$$

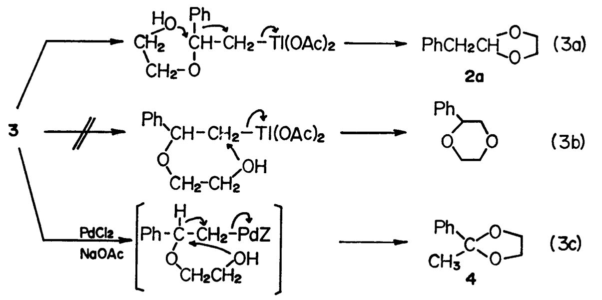
1a($\mathrm{R^1=R^2=H}$)
b($\mathrm{R^1=Me, R^2=H}$)
c($\mathrm{R^1=H, R^2=Me}$)

2a($\mathrm{R^1=R^2=H}$, n=2)
b($\mathrm{R^1=Me, R^2=H}$, n=2)
c($\mathrm{R^1=H, R^2=Me}$, n=2)
d($\mathrm{R^1=R^2=H}$, n=3)
e($\mathrm{R^1=R^2=H}$, n=4)

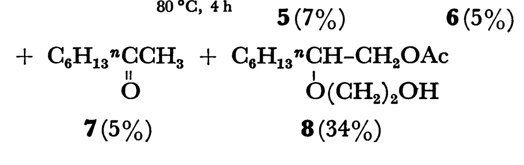


$$\mathrm{Ph\text{-}CH{=}CH_2} \xrightarrow[\mathrm{HO(CH_2)_2OH},\ 15\text{—}25\,°\mathrm{C},\ 20\,\mathrm{h}]{\mathrm{Tl(OAc)_3}} \underset{\mathbf{3}}{\mathrm{Ph\text{-}\underset{\underset{\displaystyle OCH_2CH_2OH}{|}}{C}H\text{-}CH_2Tl(OAc)_2}} + \underset{\mathbf{2a}}{\mathrm{PhCH_2CH\genfrac{}{}{0pt}{}{\diagup O\text{-}CH_2}{\diagdown O\text{-}CH_2}}} \quad (2)$$

This indicates that **2a** was formed through a 1,2-shift of the phenyl group with dethallation and a simultaneous or successive nucleophilic attack of hydroxy oxygen on the carbon bearing alkoxyl group (Scheme 3a) as was noted in thermal decomposition of methoxythallate of styrene in methanol,[3c)] with no intramolecular attack of oxygen on carbon bearing thallium moiety to give 2-phenyl-1,4-dioxane (Scheme 3b) taking place at all. Formation of **2b**—**e** can also be explained by a similar scheme. On the other hand, when **3** was heated in 1,2-ethanediol in the presence of palladium(II) salt, 2-methyl-2-phenyl-1,3-dioxolane (**4**) was readily obtained almost quantitatively. Formation of **4** can be explained by Scheme 3c which involves hydride shift instead of phenyl migration as has been proposed in the reactions of alkoxymercurials[2b)] and alkoxythallates[3a)] of olefins with palladium(II) salts.



If the phenyl group which easily migrates to give **2a**—**e** is replaced by the alkyl group, the formation of the reaction product by Scheme 3b can be expected since the alkyl group does not migrate as easily as the phenyl group. We chose 1-octene as a substrate and carried out its oxidation in 1,2-ethanediol at 80 °C for 4 h, the oxidation with thallium(III) acetate in methanol having been reported in detail.[4)] As a result one major product and three minor ones were identified (Scheme 4) together with smaller amounts of some



$$\mathrm{C_6H_{13}{}^nCH{=}CH_2} \xrightarrow[\mathrm{HO(CH_2)_2OH},\ 80\,°\mathrm{C},\ 4\,\mathrm{h}]{\mathrm{Tl(OAc)_3}} \underset{\mathbf{5}(7\%)}{\mathrm{C_6H_{13}{}^n\text{-dioxane}}} + \underset{\mathbf{6}(5\%)}{\mathrm{C_6H_{13}{}^n,CH_3\text{-dioxolane}}} + \underset{\mathbf{7}(5\%)}{\mathrm{C_6H_{13}{}^n\overset{}{\underset{\underset{\displaystyle O}{\|}}{C}}CH_3}} + \underset{\mathbf{8}(34\%)}{\mathrm{C_6H_{13}{}^n\underset{\underset{\displaystyle O(CH_2)_2OH}{|}}{C}H\text{-}CH_2OAc}} \quad (4)$$

---

*To whom correspondence should be addressed.

unidentified compounds. 2-Heptyl-1,3-dioxolane or 1-octanal which arises from hexyl group migration was not formed in the reaction products. Formation of 2-hexyl-1,4-dioxane (**5**) shows that the reaction corresponding to Scheme 3b is partly operative in this case. A similar reaction in 1,3-propanediol gave no compound corresponding to **5**.

Although thallium(III) was almost completely reduced to thallium(I) in these reactions, the yields of the products were generally low. This may be due to the consumption of thallium(III) for the oxidation of diols as was noted by Kabbe in the case of some 1,2-diols.[5] We also confirmed that when thallium(III) acetate (10 mmol) is heated in 1,2-ethanediol (7.5 ml) at 82 °C for 4 h, 65% of thallium(III) is reduced to thallium(I) (by iodometry).

Experimental

Commercial organic and inorganic materials were used. The IR and NMR spectra were recorded with a Hitachi EPI-S2 and a Varian EM-360 apparatus, respectively. Gas chromatography was carried out on Shimadzu 4BMPF and 5APTF apparatus using EGSS-X(15%)-Chromosorb-W (1 m and 3 m) and PEG-6000(25%)-Chromosorb-W (3 m) columns (N_2 as a carrier gas).

Oxidation of Olefin with $Tl(OAc)_3$ in Diol. A typical experimental procedure is as follows. A mixture of styrene (4.1 g, 40 mmol), $Tl(OAc)_3$ (7.7 g, 20 mmol), and 1,2-ethanediol (15 ml) was heated at 80 °C for 4 h under stirring. After the usual work-up, GLC analysis of benzene extract revealed the presence of 7.2 mmol (36% yield based on Tl^{3+} charged) of 2-benzyl-1,3-dioxolane (**2a**) and small amounts of phenylacetaldehyde and acetophenone as the products, butyrophenone being used as an internal standard. Distillation gave 0.5 g of pure **2a**. Thallium(III) was almost completely reduced to thallium(I). Authentic samples of **2a**—**e**, **4**, and **6** were prepared by the acetalization or ketalization of phenylacetaldehyde, 2-phenylpropionaldehyde, acetophenone and 2-octanone in the corresponding diols[6] and their structures were confirmed by NMR; **2a** bp 80—93 °C/2 Torr, **2b** bp 81 °C/2 Torr, **2c** bp 93—95 °C/4 Torr, **2d** bp 100—104.5 °C/4 Torr, **2e** bp 106—110 °C/4 Torr, **4** bp 83—84 °C/15 Torr, **6** bp 78—79°C/15 Torr. **5** was prepared by the alkaline dehydrobromination of 1-bromo-2-(2-hydroxyethoxy)octane which was synthesized from 1-octene, 1,2-ethanediol, and *N*-bromosuccinimide.[7] **8** was prepared by the reaction of 1-bromo-2-(2-hydroxyethoxy)octane with KOAc in DMSO; bp 120—123 °C/5 Torr, NMR (CCl_4) δ 0.67—1.07 (m. 3H), 1.07—1.73 (m. 10H), 1.98(s. 3H), 2.3(br. 1H), 3.23—3.67(m. 5H), and 3.67—4.23(m. 2H). No 2-acetoxy-1-(2-hydroxyethoxy)octane (positional isomer of **8**) was detected by NMR in the oxidation products of 1-octene.

*Isolation of **3**.* A mixture of styrene (4.1 g, 40 mmol), $Tl(OAc)_3$ (7.7 g, 20 mmol), and 1,2-ethanediol (15 ml) was stirred at 15—25 °C for 20 h. To this was added 500 ml of petroleum ether and the mixture was then left to stand for 3 days in a refrigerator to give a white crystal of **3** as a precipitate. **3** was collected by filtration [4.2 g, 43% yield; mp 133—135 °C(dec)]. The treatment of organic filtrate as described above revealed the presence of 28% yield of **2a**. **3** is soluble in pyridine, DMSO, DMF, hot $CHCl_3$, and hot ethanol, but insoluble in water, THF, ether, benzene, CCl_4, acetonitrile, and acetic acid. IR(hexachlorobutadiene and paraffin mulls): 3250(s), 2950(m), 2920(m), 2860(m), 1625(sh), 1610(s), 1530(s), 1430(s), 1360(s), 1320(s), 1110(m), 1090(m), 1067(m), 974(m), 762(m), 695(m), and 685(m) cm^{-1}. NMR(pyridine-d_5): δ 2.09(s. 6H), 3.10(d. 1H, $J_{Tl-H}=732$ Hz), 3.14(d. 1H, $J_{Tl-H}=875$ Hz), 3.53(t. 2H), 3.76 (t. 2H), 5.01(d. 1H, $J_{Tl-H}=739$ Hz), 5.76(s. 1H), and 6.9—7.6 (m. 5H). Found: C, 34.48; H, 4.11; Tl, 41.28%. Calcd for $C_{14}H_{19}O_6Tl$: C, 34.48; H, 3.93; Tl, 41.91%.

*Reaction of **3** with Palladium(II) Salt.* **3** (0.98 g, 2 mmol) was added to a hot mixture (75—80 °C) of $PdCl_2$ (0.36 g, 2.03 mmol), NaOAc (0.33 g, 4.02 mmol), and 1,2-ethanediol (10 ml) and the resulting mixture was stirred for 20 min. A black precipitate formed was filtered off. Saturated aq. NaCl was added to the filtrate which was then extracted with benzene. GLC analysis of the benzene extract revealed the presence of acetophenone (0.19 mmol) and 2-methyl-2-phenyl-1,3-dioxolane (**4**, 1.81 mmol) together with a trace amount of **2a**, *p*-methylacetophenone being used as an internal standard.

References

1) Presented at the 33rd Annual Meeting of the Chemical Society of Japan, Fukuoka, October 19, 1975.

2) a) R. Jira and W. Freiesleben, "Organometallic Reactions," Vol. 3, ed. by E. I. Becker and M. Tsutsui, Wiley-Interscience, New York, N. Y. (1972), pp. 157—158; b) D. F. Hunt and G. T. Rodeheaver, *Tetrahedron Lett.*, **1972**, 3595.

3) a) S. Uemura, K. Zushi, M. Okano, and K. Ichikawa, *J. Chem. Soc., Chem. Commun.*, **1972**, 234; b) S. Uemura, A. Tabata, and M. Okano, *J. Chem. Soc., Chem. Commun.*, **1972**, 517; c) S. Uemura, K. Zushi, A. Tabata, A. Toshimitsu, and M. Okano, *Bull. Chem. Soc. Jpn.*, **47**, 920 (1974); d) S. Uemura, A. Toshimitsu, M. Okano, and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **48**, 1925 (1975).

4) A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1929.

5) H. J. Kabbe, *Justus Liebigs Ann. Chem.*, **656**, 204 (1962).

6) S. R. Sandler and W. Karo, "Organic Functional Group Preparations," Part III, Academic Press, New York, N. Y. (1972), Chap. 1.

7) A. Iovchev, H. Reinheckel, L. Stoilov, and K. Haage, *Monatsh. Chem.*, **102**, 114 (1971).