

SHORT  
COMMUNICATIONS

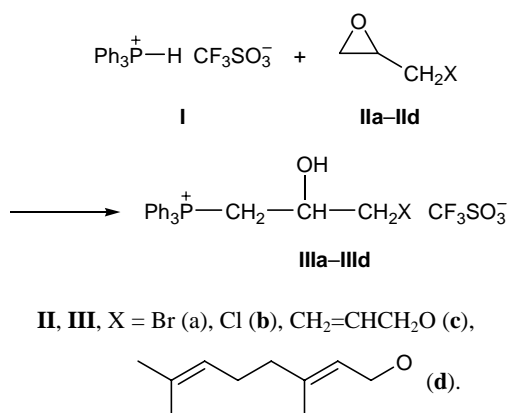
## Triphenylphosphonium Trifluoromethanesulfonate in Reactions with Epoxy Derivatives

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It is known that three-component reactions between trialkylphosphine, OH acid, and epoxy compound occur under mild conditions and lead to phosphonium salts containing a hydroxy group in the  $\alpha$ -position in a fairly high yield. Here, the first reaction step includes opening of the oxirane ring by the action of acid, which is followed by reaction with phosphine [1]. Phosphonium salts derived from such a strong acid as trifluoromethanesulfonic acid, are capable of adding at multiple phosphorus–carbon bonds like PH acids without preliminary dissociation into the corresponding phosphine and acid [2]. In the present communication we are the first to demonstrate that triphenylphosphonium trifluoromethanesulfonate (**I**) reacts under mild conditions (methylene chloride,  $-20$  to  $0^\circ\text{C}$ ) with epoxy derivatives **II**. The reactions occur with high regioselectivity, and opening of the oxirane ring in compounds **II** leads to formation of  $\alpha$ -hydroxyalkyltriphenylphosphonium trifluoromethanesulfonates **III** in good yields. These reactions provide a mild procedure for synthesizing phosphonates as potential physiologically active substances on the basis of ethylene glycol derivatives.



**3-Bromo-2-hydroxypropyltriphenylphosphonium trifluoromethanesulfonate (IIIa).** Trifluoromethanesulfonic acid, 1.37 ml, was added dropwise with stirring at  $0^\circ\text{C}$  under argon to a solution of 3.15 g of triphenylphosphine in 40 ml of methylene chloride. The mixture was cooled to  $-10^\circ\text{C}$ , and 2 g of 1-bromo-2,3-epoxypropane (**IIa**) was added with stirring. The mixture was allowed to warm up to  $20^\circ\text{C}$  (30–40 min) and evaporated under reduced pressure (12 mm); the viscous slightly yellowish residue crystallized with time. The crystals were washed with anhydrous diethyl ether and dried. Yield 95%, mp  $165$ – $166^\circ\text{C}$  (from methanol).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 7.67–7.77 m ( $\text{C}_6\text{H}_5$ ); 4.16 m ( $\text{H}_M$ ); 3.66–3.70 m ( $\text{CH}_2\text{Br}$ ,  $^3J_{M,\text{CH}} = 5.4$  Hz;  $\text{H}_B$ ,  $^2J_{AB} = 14.7$ ,  $^3J_{P,B} = 11.9$ ,  $^3J_{MB} = 11.0$  Hz); 3.44 d.d.d ( $^2J_{BA} = 14.7$ ,  $^3J_{PA} = 13.6$ ,  $^3J_{MA} = 2.4$  Hz).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\delta_P$  24.5 ppm. Found, %: C 48.41; H 3.93.  $\text{C}_{22}\text{H}_{21}\text{BrF}_3\text{PO}_4\text{S}$ . Calculated, %: C 48.09; H 3.82.

Compounds **IIIb–IIIId** were synthesized following an analogous procedure.

**3-Chloro-2-hydroxypropyltriphenylphosphonium trifluoromethanesulfonate (IIIb).** Yield 92%, mp  $154$ – $155^\circ\text{C}$  (from acetone). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3365–3370 v.br, s (O–H); 1585, 1482, 1480, 1340, 1315, 1285 v.s, 1260 sh, 1255, 1225, 1199, 1180, 1176, 1113, 1085, 1030, 1002, 928, 841, 790, 755, 750, 725, 713, 680, 645, 575, 535, 520, 510, 498, 466.  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{OD}$ ),  $\delta$ , ppm: 7.94–8.03 m ( $\text{C}_6\text{H}_5$ ); 4.24 m ( $\text{H}_M$ ); 4.09 d.d.d ( $\text{H}_B$ ,  $^2J_{AB} = 15.1$ ,  $^2J_{P,B} = 11.9$ ,  $^3J_{MB} = 10.8$  Hz); 3.91–3.94 m ( $AB$  part of the  $ABMX$  system,  $^2J_{AB} = 11.3$ ,  $^3J_{MA} = 5.3$ ,  $^4J_{PA} = 1.5$ ,  $^3J_{MB} = 4.5$ ,  $^4J_{P,B} = 1.9$  Hz); 3.78 d.d.d ( $\text{H}_B$ ,  $^2J_{BA} = 15.1$ ,  $^2J_{PA} = 14.0$ ,  $^3J_{MA} = 2.8$  Hz).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\delta_P$  22.5 ppm. Found, %: C 52.47; H 4.31.  $\text{C}_{22}\text{H}_{21}\text{ClF}_3\text{PO}_4\text{S}$ . Calculated, %: C 52.33; H 4.16.

**2-Hydroxy-3-(2-propenyloxy)propyltriphenylphosphonium trifluoromethanesulfonate (IIIc).**

Yield 87%, mp 124–125°C (from CH<sub>2</sub>Cl<sub>2</sub>–benzene). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3370–3390 v.br, s (O–H); 1615, 1590, 1488, 1440, 1355, 1340, 1305 sh, 1290, 1250, 1230, 1175, 1160, 1115, 1054, 1033, 1001, 940, 890, 855, 845, 796, 755, 726, 717, 695, 643, 575, 541, 515, 500, 480. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD),  $\delta$ , ppm: 7.90–8.02 m (C<sub>6</sub>H<sub>5</sub>); 6.11 d.d.t (=CH, <sup>3</sup>J<sub>trans</sub> = 17.3, <sup>3</sup>J<sub>cis</sub> = 10.4, <sup>3</sup>J<sub>HH</sub> = 5.6 Hz); 5.47 d.d.t (=CH, <sup>3</sup>J<sub>trans</sub> = 17.3, <sup>2</sup>J<sub>HH</sub> = 1.6, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz); 5.36 d.d.t (=CH, <sup>3</sup>J<sub>cis</sub> = 10.4, <sup>2</sup>J<sub>HH</sub> = 1.6, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz); 4.18 m (CHOH, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz); 3.95 d.d.d (PCH<sub>B</sub>, <sup>2</sup>J<sub>AB</sub> = 15.5, <sup>2</sup>J<sub>P,B</sub> = 11.5, <sup>3</sup>J<sub>B,CH</sub> = 10.6 Hz); 3.74 m (=CCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 5.6, <sup>4</sup>J<sub>cis</sub> = 1.5, <sup>4</sup>J<sub>trans</sub> = 1.3 Hz); 3.69 d.d.d (PCH<sub>A</sub>, <sup>2</sup>J<sub>BA</sub> = 15.5, <sup>2</sup>J<sub>PA</sub> = 13.8, <sup>3</sup>J<sub>A,CH</sub> = 2.7 Hz). <sup>31</sup>P–{<sup>1</sup>H} NMR spectrum (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  23.5 ppm. Found, %: C 56.97; H 5.12. C<sub>25</sub>H<sub>26</sub>F<sub>3</sub>PO<sub>5</sub>S. Calculated, %: C 57.03; H 4.94.

**2-Hydroxy-3-(3,7-dimethyl-2,6-octadienyloxy)propyltriphenylphosphonium trifluoromethanesul-**

**fonate (IIIId).** Oily liquid, yield 89%. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3420 v.br (O–H); 3063 m (C–H<sub>arom</sub>); 1658 w, 1637 w (C=C); 1580 m, 1480 m, 1435 (C=C<sub>arom</sub>); 1038 s (CH–O–C). <sup>31</sup>P–{<sup>1</sup>H} NMR spectrum (ethyl acetate):  $\delta$ <sub>p</sub> 24.1 ppm. Found, %: C 63.77; H 5.71. C<sub>32</sub>H<sub>33</sub>F<sub>3</sub>PO<sub>4</sub>S. Calculated, %: C 63.89; H 5.49.

The <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker MSL-400 spectrometer (400 and 162.0 MHz, respectively).

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## REFERENCES

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