

## A Convenient Method for the Synthesis of 2-Oxoalkylidetriphenylphosphoranes

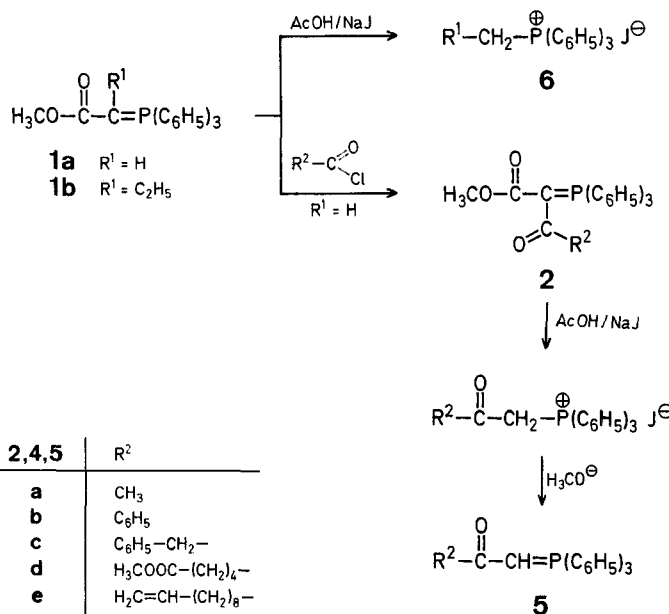
Gábor DOLESCHALL

Research Group for Alkaloid Chemistry, Hungarian Academy of Sciences, H-1521 Budapest, Hungary

The synthetically useful 2-oxoalkylidetriphenylphosphoranes [5, (acylmethylene)-triphenylphosphoranes] are generally prepared by two routes: reaction of triphenylphosphine with  $\alpha$ -haloketones and treatment of the resultant phosphonium salts with alkali, or acylation of methylenetriphenylphosphorane<sup>1</sup> with acyl chlorides<sup>2</sup> or active carboxylic acid derivatives<sup>3</sup>. This latter method can be generalized; we present here a simplified modification which may serve as an alternative and avoids the use of methylenetriphenylphosphorane and in which the readily available, more convenient to handle (methoxycarbonylmethylene)-triphenylphosphorane<sup>4</sup> (**1a**) is used as starting material.

(Methoxycarbonylmethylene)-triphenylphosphorane (**1a**) can be easily acylated<sup>5,6</sup>; however, removal of the methoxycarbonyl group from the resultant 1-methoxycarbonyl-2-oxoalkylidetriphenylphosphorane (**2**) could so far not be accomplished because compounds **2** are rather stable in alkaline and neutral medium whereas in acidic medium they are reconverted into the starting phosphonium chloride **3**<sup>6</sup>. In our present procedure, the methoxycarbonyl group of **2** is removed by refluxing in 99.5% acetic acid in the presence of sodium iodide. In the absence of sodium iodide, long reaction times (8 h) are required for the cleavage. The phosphonium iodides **4** obtained in this manner are converted into the desired 2-oxoalkylidetriphenylphosphoranes (**5**) in the usual way<sup>1</sup> by treatment with aqueous alkali. During the whole process, the use of an inert atmosphere or a strong base (butyllithium, phenyllithium, potassium *t*-butoxide) is not required.

The reaction of 1-methoxycarbonylalkylidetriphenylphosphoranes (e.g. **1b**) with acetic acid and sodium iodide affords alkyl-triphenylphosphonium iodides (**6**). Since the alkylation of **1a** is known<sup>7</sup> this process provides further synthetic possibilities.



Melting points, determined with a Boetius PHMK-05 apparatus, are uncorrected. I.R. spectra were recorded with a Spectromom 2000 spectrometer (Hungarian Optical Works, Budapest), the 60 MHz <sup>1</sup>H-N.M.R. spectra with a Perkin-Elmer R-20 spectrometer.

#### 1-Methoxycarbonyl-2-oxoalkylidetriphenylphosphoranes (2); General Procedure:

(Methoxycarbonylmethylene)-triphenylphosphorane (**1a**) is acylated with the acyl chloride as described in Ref.<sup>5</sup>.

**1,6-Dimethoxycarbonyl-2-oxohexylidetriphenylphosphorane (2d)**; yield: 91%; m.p. 113 °C (ethyl acetate/pentane).

C <sub>28</sub> H <sub>29</sub> O <sub>3</sub> P	calc.	C 70.58	H 6.14
(476.5)	found	70.77	6.44

I.R. (KBr): ν = 1740, 1660, 1550 cm<sup>-1</sup>.

<sup>1</sup>H-N.M.R. (CDCl<sub>3</sub>/TMS): δ = 1.8–2.4 [m, 6H, (CH<sub>2</sub>)<sub>3</sub>]; 2.95 (t, 2H, CH<sub>2</sub>-CO); 3.15 (s, 3H, OCH<sub>3</sub>); 7.4–7.8 ppm (m, 15H<sub>arom</sub>).

**1-Methoxycarbonyl-2-oxo-11-dodecylidetriphenylphosphorane (2e)**; yield: 93%; oil.

C <sub>32</sub> H <sub>37</sub> O <sub>3</sub> P	calc.	C 76.77	H 7.45
(500.6)	found	76.58	7.22

I.R. (KBr): ν = 1660, 1550 cm<sup>-1</sup>.

<sup>1</sup>H-N.M.R. (CDCl<sub>3</sub>/TMS): δ = 1.2–1.5 [m, 12H, (CH<sub>2</sub>)<sub>6</sub>]; 1.7–1.9 (m, 2H, -CH<sub>2</sub>-CH-); 2.75 (t, 2H, CH<sub>2</sub>-CO); 2.95 (s, 3H, OCH<sub>3</sub>); 4.6–4.9 (m, 2H, H<sub>2</sub>C=C); 5.3–5.8 (m, 1H, -CH); 7.1–7.7 ppm (m, 15H<sub>arom</sub>).

#### 2-Oxoalkyltriphenylphosphonium Iodides (4); General Procedure:

A mixture of a phosphorane **2** (15 mmol), 99.5% acetic acid (50 ml), and sodium iodide (4.5 g, 30 mmol) is refluxed for 2 h and then evaporated in vacuo. The residue is stirred with methanol (25 ml) and a solution of potassium iodide (10 g) in water (100 ml) is added. The suspension is extracted with dichloromethane (3 × 50 ml), washed with water (2 × 80 ml), and evaporated in vacuum. To the residue, dichloromethane (80 ml) and heptane (80 ml) are added, the solvent is again evaporated in vacuo, and the residue is triturated with ether (30 ml), isolated by suction, and dried in air.

**2-Oxopropyltriphenylphosphonium Iodide (4a)**; yield: 82%; m.p. 207–209 °C (Ref.<sup>8</sup>, m.p. 207–209 °C).

**Phenacyltriphenylphosphonium Iodide (4b)**; yield: 97%; m.p. 259–260 °C (Ref.<sup>8</sup>, m.p. 259–260 °C).

**2-Oxo-3-phenylpropyltriphenylphosphonium Iodide (4c)**; yield: 89%; dec. > 140 °C (methanol).

C <sub>27</sub> H <sub>24</sub> JOP	calc.	C 62.08	H 4.63	J 24.30
(522.3)	found	62.18	4.92	24.50

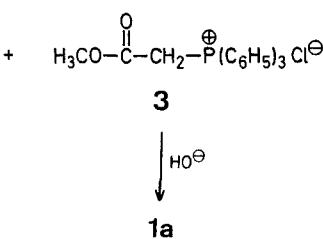
I.R. (KBr): ν = 1705, 1580 (w), 1480 (w) cm<sup>-1</sup>.

<sup>1</sup>H-N.M.R. (DMSO-*d*<sub>6</sub>/TMS): δ = 4.1 (s, 2H, CH<sub>2</sub>-CO); 5.75 (d, 2H, J = 13.3 Hz, CH<sub>2</sub>-P); 7.2–7.8 ppm (m, 20H<sub>arom</sub>).

**6-Methoxycarbonyl-2-oxohexyltriphenylphosphonium Iodide (4d)**; yield: 87%; m.p. 179 °C (2-propanol).

C <sub>26</sub> H <sub>28</sub> JOP	calc.	C 57.13	H 5.16	J 23.23
(546.4)	found	57.33	5.16	23.30

I.R. (KBr): ν = 1740, 1720, 1580 (w), 1480 (w) cm<sup>-1</sup>.



<sup>1</sup>H-N.M.R. (CDCl<sub>3</sub>/TMS): δ = 1.4–2.4 [m, 6H, (CH<sub>2</sub>)<sub>3</sub>]; 3.05 (t, 2H, CH<sub>2</sub>-CO); 3.50 (s, 3H, OCH<sub>3</sub>); 5.65 (d, 2H, J = 13.3 Hz, CH<sub>2</sub>-P); 7.5–8.0 ppm (m, 15H<sub>arom</sub>).

**2-Oxo-11-dodecyltriphenylphosphonium Iodide (4e)**; yield: 67%; m.p. 92–93 °C (ethyl acetate).

C <sub>30</sub> H <sub>30</sub> JOP	calc.	C 63.16	H 6.36	J 22.25
(570.5)	found	63.34	6.58	22.39

I.R. (KBr): ν = 1705, 1620 (w), 1580 (w), 1480 (w) cm<sup>-1</sup>.

<sup>1</sup>H-N.M.R. (CDCl<sub>3</sub>/TMS): δ = 1.2–1.8 [m, 12H, (CH<sub>2</sub>)<sub>6</sub>]; 1.9–2.1 (m, 2H, -CH<sub>2</sub>-CH-); 2.95 (t, 2H, CH<sub>2</sub>-CO); 4.6–4.9 (m, 2H, H<sub>2</sub>C=C); 5.3–5.8 (m, 1H, CH); 5.65 (d, 2H, J = 13.3 Hz, CH<sub>2</sub>-P); 7.6–7.8 ppm (m, 15H<sub>arom</sub>).

#### Methyltriphenylphosphonium Iodide (6a):

Prepared from **1a** following the general procedure given for iodides **4**; yield of **6a**: 87%; m.p. 182–183 °C (Ref.<sup>9</sup>, m.p. 182–183 °C).

#### Propyltriphenylphosphonium Iodide (6b):

Prepared from **1b** (this is obtained from **1a** and ethyl iodide according to Ref.<sup>7,10</sup>) following the general procedure given for iodides **4**; yield of **6b**: 90%; m.p. 201 °C (Ref.<sup>11</sup>, m.p. 201 °C).

#### 2-Oxoalkylidetriphenylphosphoranes (5); General Procedure:

The 2-oxoalkylphosphonium iodide **4** (10 mmol) is stirred with methanol (20 ml) and a solution of sodium methoxide (10 mmol) in methanol (10 ml) is added. After 5 min, water (150 ml) is added to the mixture and the precipitate is extracted with ether (120 ml). The ether solution is washed with water (80 ml) and the ether is removed by distillation. The residue is crystallized from benzene/pentane.

**2-Oxopropylidetriphenylphosphorane (5a)**; yield: 95%; m.p. 205–206 °C (Ref.<sup>8</sup>, m.p. 205–206 °C).

**Phenacylidetriphenylphosphorane (5b)**; yield: 97%; m.p. 178–180 °C (Ref.<sup>8</sup>, m.p. 178–180 °C).

**2-Oxo-3-phenylpropylidetriphenylphosphorane (5c)**; yield: 85%; m.p. 98–99 °C (Ref.<sup>8</sup>, m.p. 98–99 °C).

**6-Methoxycarbonyl-2-oxohexylidetriphenylphosphorane (5d)**; yield: 95%; m.p. 108 °C (Ref.<sup>12</sup>, m.p. 108 °C).

**2-Oxo-11-dodecylidetriphenylphosphorane (5e)**; yield: 98%; m.p. 64–65 °C (heptane).

C <sub>30</sub> H <sub>35</sub> OP	calc.	C 81.41	H 7.97
(442.6)	found	81.30	8.21

I.R. (KBr): ν = 1640 (w), 1540, 1480 (w) cm<sup>-1</sup>.

<sup>1</sup>H-N.M.R. (CDCl<sub>3</sub>/TMS): δ = 1.2–2.2 [m, 16H, (CH<sub>2</sub>)<sub>8</sub>]; 3.55 (d, 1H, J = 27 Hz, CH=P); 4.6–4.9 (m, 2H, H<sub>2</sub>C=C); 5.3–5.8 (m, 1H, CH); 7.2–7.8 ppm (m, 15H<sub>arom</sub>).

The author wishes to thank Dr. I. Balogh and Mss. L. Török for the microanalyses, Dr. P. Kolonits and staff for the I.R. and <sup>1</sup>H-N.M.R. spectra.

Received: August 22, 1980  
 (Revised form: November 10, 1980)

<sup>1</sup> A. Maercker, *Org. React.* **14**, 270 (1965).

- <sup>2</sup> H. J. Bestmann, H. Schulz, *Angew. Chem.* **73**, 27 (1961).  
<sup>3</sup> H. J. Bestmann, B. Arnason, *Chem. Ber.* **95**, 1513 (1962).  
<sup>4</sup> O. Isler et al., *Helv. Chim. Acta* **40**, 1242 (1957).  
<sup>5</sup> G. Märkl, *Chem. Ber.* **94**, 3005 (1961).  
<sup>6</sup> P. A. Chopperd, R. J. Searle, F. H. Devitt, *J. Org. Chem.* **30**, 1015 (1965).  
<sup>7</sup> H. J. Bestmann, H. Schulz, *Chem. Ber.* **95**, 2921 (1962).  
<sup>8</sup> F. Ramirez, S. Dershowitz, *J. Org. Chem.* **22**, 41 (1954).  
<sup>9</sup> A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **52**, 1556 (1915).  
<sup>10</sup> H. J. Bestmann, H. Schulz, *Justus Liebigs Ann. Chem.* **674**, 11 (1964).  
<sup>11</sup> P. Senise, L. R. M. Pitombo, *An. Assoc. Bras. Quim.* **20**, 93 (1961); *C. A.* **58**, 1487 (1963).  
<sup>12</sup> H. Oediger, L. Folker, *German Patent (DOS)* 2711008 (1977), Bayer AG; *C. A.* **89**, 215552 (1978).

0039-7881/81/0632-0480 \$ 03.00

© 1981 Georg Thieme Verlag · Stuttgart · New York