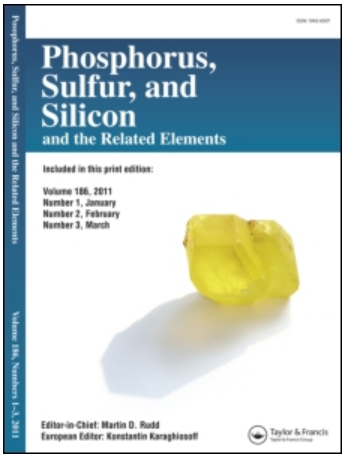



**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# A NEW SYNTHETIC APPROACH TO α,β-UNSATURATED PHOSPHONATES (1-METHYLENEALKANE-PHOSPHONATES)

S. Inokawa[a]; H. Yamamoto[a]
[a] Department of Chemistry, Faculty of Science, Okayama University, Okayama, Japan

**To cite this Article** Inokawa, S. and Yamamoto, H.(1983) 'A NEW SYNTHETIC APPROACH TO α,β-UNSATURATED PHOSPHONATES (1-METHYLENEALKANE-PHOSPHONATES)', Phosphorus, Sulfur, and Silicon and the Related Elements, 16: 1, 79 — 81
**To link to this Article: DOI:** 10.1080/03086648308077754
**URL:** http://dx.doi.org/10.1080/03086648308077754

*Phosphorus and Sulfur*, 1983, Vol. 16, pp. 79–81
0308-664X/83/1601-0079/$18.50/0



# A NEW SYNTHETIC APPROACH TO α,β-UNSATURATED PHOSPHONATES (1-METHYLENEALKANE-PHOSPHONATES)

S. INOKAWA and H. YAMAMOTO

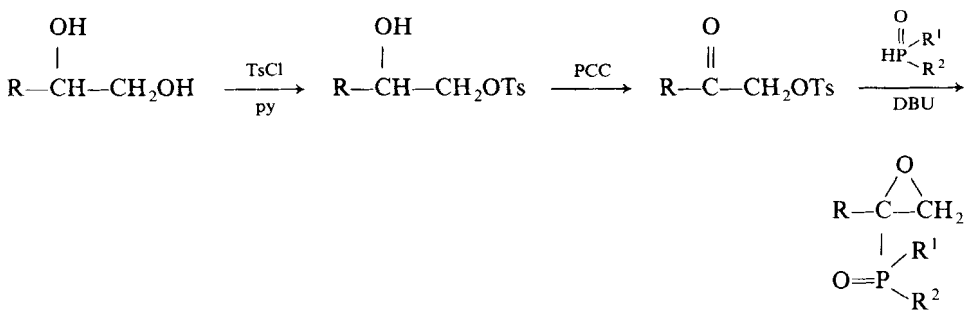
*Department of Chemistry, Faculty of Science, Okayama University, Okayama, 700 Japan*

(*Received December 15, 1982*)

α,β-Unsaturated phosphonates were prepared in good yields by refluxing 1,2-epoxy-1-alkylethanephosphonates in methanol with thiourea (5 equiv.) for 4 hours.

Many methods[1-5] for the preparation of α,β-unsaturated phosphonates have been reported but these procedures are rather complicated or the yields are sometimes poor.

In the course of our studies on the phosphorus-sugars, we have found a convenient and very mild method for the preparation of 1,2-epoxy-1-alkylethanephosphonates (phosphinate).[6-9]

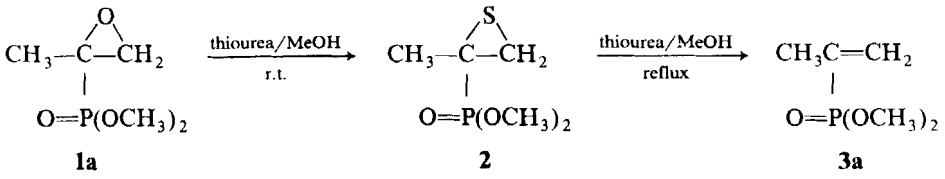


PCC: pyridinium chlorochromate
DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene

We have now used these easily obtainable 1,2-epoxy-1-alkylphosphonates (phosphinate) **1** as starting materials, and we have prepared α,β-unsaturated phosphonates (phosphinate) in moderate yields under mild conditions.

Dimethyl 1,2-epoxy-1-methylethanephosphonate **1a** in methanol was treated with thiourea (2 equiv.) at room temperature for 4 hours to give dimethyl 1,2-epithio-1-methylethanephosphonate **2** in an almost quantitative yield as determined by its $^1$H-N.M.R. spectrum. Compound **2** in methanol was heated under reflux with thiourea (4 equiv.) to give dimethyl isopropenylphosphonate **3a** in an almost quantitative yield as determined by $^1$H-N.M.R..

Alternatively, **3a** was prepared directly by refluxing **1a** in methanol with thiourea (5 equiv.) for 4 hours in an almost quantitative yield by $^1$H-N.M.R. spectroscopy and in 85% yield after distillation.




**1a** **2** **3a**


**1a,b,c,d,** **3a,b,c,d**

**a**: R = $CH_3$, $R^1 = R^2 = OCH_3$

**b**: R = $CH_3$, $R^1 = R^2 = OCH_2CH_3$

**c**: R = c-$C_6H_{11}$, $R^1 = R^2 = OCH_3$

**d**: R = c-$C_6H_{11}$, $R^1$ = Ph, $R^2 = OCH_2CH_3$

Similarly, diethyl isopropenylphosphonate **3b**, dimethyl 1-cyclohexylvinylphosphonate **3c**, and ethyl (1-cyclohexylvinyl)phenylphosphinate **3d** were prepared in good yields from diethyl 1,2-epoxy-1-methylethanephosphonate **1b**, dimethyl 1,2-epoxy-1-cyclohexylethanephosphonate **1c**, and ethyl (1,2-epoxy-1-cyclohexylethyl)phenylphosphinate **1d**, respectively.

## EXPERIMENTAL

$^1$H-N.M.R. spectra in $CCl_4$ solution were recorded with an Hitachi-Perkin-Elmer R-20A (60 MHz) spectrometer. Chemical shifts in ppm are reported relative to tetramethylsilane ($\delta$ 0.0) as the internal standard.

TABLE I

Yields, boiling points, elemental analyses, and $^1$H-N.M.R. data for **1a–1d**

| Compound | Yield (%) | b.p. (°C/mm) | Lit. b.p. (°C/mm) | Required C | Required H | Found C | Found H |
|---|---|---|---|---|---|---|---|
| **1a** | 86 | 60/0.1 | 60/0.1[9] | — | — | — | — |
| **1b** | 90 | 59–61/0.1 | 75.5–77/1.5[10] | — | — | — | — |
| **1c** | 72 | 93–94/0.1 | — | 51.27 | 8.17 | 51.02 | 8.14 |
| **1d** | 62 | 132–134/0.1 | — | 65.29 | 7.87 | 64.97 | 7.81 |

| Compound | $^1$H-N.M.R. ($CCl_4$) $\delta$ (ppm) |
|---|---|
| **1c** | 0.8–2.0 (m, 11 H, c-$C_6H_{11}$); 2.68, 2.90 (t, t, 2 H, $J_{gem\text{-}H} = J_{cis\text{-}PH} = J_{trans\text{-}PH}$ 5.5 Hz, $CH_2$); 3.67 (d, 6 H, $J_{PH}$ 10.2 Hz, $POCH_3$) |
| **1d** | 1.21, 1.28 (t, t, 3 H, $J_{HH}$ 6.8 Hz, $POCCH_3$); 0.8–2.2 (m, 11 H, c-$C_6H_{11}$); 2.31, 2.59, 2.79, 3.04 (t, t, t, t, 2 H, $J_{gem\text{-}H} = J_{cis\text{-}PH} = J_{trans\text{-}PH}$ 5.1 Hz, $CH_2$); 3.6–4.3 (m, 2 H, $POCH_2C$), 7.1–8.1 (m, 5 H, $C_6H_5$) |

TABLE II

Yields, boiling points, elemental analyses, and $^1$H-N.M.R. data for **3a–3d**

| Compound | Yield (%) | b.p. (°C/mm) | Lit. b.p. (°C/mm) | Required C | Required H | Found C | Found H |
|---|---|---|---|---|---|---|---|
| **3a** | 85 | 38–40/1 | 38–41/1[3] | — | — | — | — |
| **3b** | 85 | 49–51/1 | 46–47/1[5] | — | — | — | — |
| **3c** | 79 | 82–83/1 | 80–81/1[5] | — | — | — | — |
| **3d** | 67 | 129–132/0.1 | — | 69.54 | 8.39 | 69.05 | 8.33 |

| Compound | $^1$H-N.M.R. ($CCl_4$) δ (ppm) |
|---|---|
| **3d** | 1.33 (t, 3 H, $J_{HH}$ 7.0 Hz, $POCH_3$); 0.95–2.80 (m, 11 H, *c*-$C_6H_{11}$); 4.05 (d of q, 2 H, $J_{PH}$ 7.0 Hz, $POCH_2C$); 5.73 (d, 1 H, $J_{trans\text{-}PH}$ 45.2 Hz, *trans*-P=CH); 5.95 (d, 1 H, $J_{cis\text{-}PH}$ 22.0 Hz, *cis*-P=CH); 7.35–8.15 (m, 5 H, $C_6H_5$) |

*1. Starting materials.* Dimethyl 1,2-epoxy-1-methylethanephosphonate **1a**, diethyl 1,2-epoxy-1-methylethanephosphonate **1b**, dimethyl 1,2-epoxy-1-cyclohexylethanephosphonate **1c**, and ethyl (1,2-epoxy-1-cyclohexylethyl)phenylphosphonate **1d** were prepared by the method of Inokawa *et al.*[6–9] Yields and data are shown in Table I.

*2. Dimethyl 1,2-epithio-1-methylethanephosphonate* **2**. A solution of **1a** (2.0 g) in methanol (50 ml) was stirred with thiourea (1.8 g) in room temperature for 3 hours and evaporated *in vacuo*. Benzene was added, the precipitates were filtered off; the benzene solution was washed with water, dried (sodium sulfate), evaporated *in vacuo*, and distilled to give **2** (1.9 g, 86%) (b.p. 56–58°C/0.1 mm) as an oil. $^1$H-N.M.R. ($CCl_4$): δ (ppm) 1.64 (d, 3 H, $J_{PH}$ 12.1 Hz, $CH_3$); 2.35, 2.72 (d, d, 2 H, $J_{cis\text{-}PH} = J_{trans\text{-}PH}$ 10.9 Hz, $J_{gem\text{-}H}$ 0.0 Hz, $CH_2$); 3.75 (*d*, 6 H, $J_{PH}$ 10.2 Hz, $POCH_3$). Mass spectrum, m/z: 182 ($M^+$).

*3. 1-Methylenealkanephosphonates (phosphinate).* General procedure: A solution of **1** (15 mmol) in methanol (60 ml) was refluxed with thiourea (75 mmol) for 4 hours. The work-up as described for **2** gave **3** in a good yield. Yields and data are shown in Table II.



## REFERENCES


1. G. H. Jones, E. K. Hamamura and J. G. Moffat, *Tetrahedron Lett.*, **1968**, 5731.
2. C. E. Griffin and T. D. Mitchell, *J. Org. Chem.*, **30**, 1935 (1965).
3. S. Inokawa, T. Gomyo, H. Yoshida and T. Ogata, *Synthesis*, **1973**, 364.
4. J. Ide, R. Endo and S. Muramatsu, *Chem. Lett.*, **1978**, 401 and references cited therein.
5. M. Kojima, M. Yamashita, H. Yoshida and T. Ogata, *Synthesis*, **1979**, 147.
6. S. Kashino, S. Inokawa, M. Haisa, N. Yasuoka and M. Kakudo, *Acta Cryst.*, **B37**, 1672 (1981).
7. S. Inokawa, K. Yamashita, H. Kawamoto, H. Yamamota, M. Yamashita and P. Luger, *Carbohydr. Res.*, **106**, 31 (1982).
8. H. Yamamoto, Y. Nakamura, H. Kawamoto, S. Inokawa, M. Yamashita, M.-A. Arnour and T. T. Nakashima, *Carbohydr. Res.*, **102**, 185 (1982).
9. S. Inokawa, Y. Kawata, K. Yamamoto, H. Kawamoto, H. Yamamoto, K. Takagi and M. Yamashita, *Carbohydr. Res.*, **88**, 341 (1981).
10. B. A. Arbuzov, V. S. Vinogradova, N. A. Polezhaeva and A. K. Shamsutdinova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1963**, 675; *Chem. Abstr.*, **59**, 11551d (1963).