A New Route to *sec*-Alkanephosphonates

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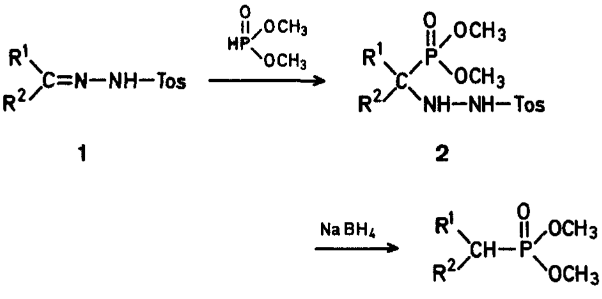
It is well known that treatment of a tosylhydrazone with a basic reagent affords an olefin[1] and reduction with complex alkali boron and aluminium hydrides yields saturated hydrocarbons via the intermediate formation of substituted tosylhydrazines[2]. Compounds of the type R—NH—NH—Tos decompose readily[2] to N_2, TosH, and R—H, and so a grouping such as —NH—NHTos is equivalent, from a chemical standpoint, to a hydrogen atom.

Working from this basis, an attempt has been made to develope a new route to *sec*-alkanephosphonates, starting from ketones according to the following scheme.



Addition of dimethyl phosphite to the tosylhydrazone **1**, obtained from the corresponding ketone, leads to a substituted tosylhydrazine **2** which, on decomposition, affords a dimethyl *sec*-alkanephosphonate **3**.

The decomposition of compounds **2** was attempted using basic reagents or thermally but the yield of **3** was low in each case. Good results were obtained by treatment with sodium borohydride in the tetrahydrofuran solution. The results are summarized in the Tables.

This method seems to be useful for the preparation of secondary alkanephosphonates, -phosphinates, and phosphine oxides which are difficult to be obtained by the Michaelis-Arbuzov reaction and the Michaelis-Becker reaction. This method also may be used for the preparation of primary phosphonates, phosphinates, and phosphine oxides from aldehydes as shown in example **e**.

Preparation of Dimethyl 1-(*N*'-Tosylhydrazino)-alkanephosphonate (2):

Tosylhydrazone **1** (15 mmol) was dissolved in a mixture of dimethyl phosphite (40 mmol) and tetrahydrofuran (20 ml) and allowed to stand at room temperature for a week to give almost pure crystalline **2**, which may be recrystallized from water/tetrahydrofuran (see Table 1).

Preparation of Dimethyl *sec*-Alkanephosphonate (3):

To **2** (15 mmol) in tetrahydrofuran (50 ml) was added sodium borohydride (50 mmol) at room temperature for 15 min, the whole was refluxed for 2 h, and allowed to stand overnight. The remaining sodium borohydride was quenched with water, the tetrahydrofuran was evaporated under reduced pressure, and the resultant mass was extracted with chloroform. The extract was washed with

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Table 1. Dimethyl 1-(*N'*-Tosylhydrazino)-alkanephosphonates (**2**)

Compund **2**	R^1	R^2	Yield [%]	m.p.	Molecular formula[a]	^{1}H-N.M.R. Spectra ($CDCl_3$) δ [ppm]
a	CH_3	CH_3	78	140°	$C_{12}H_{21}N_2O_5PS$ (336.4)	1.21 (d, 6H, $PC(CH_3)_2$, $J = 17$ Hz), 2.43 (s, 3H, $C_6H_4C\underline{H}_3$), 3.77 (d, 6H, $P(OCH_3)_2$, $J = 11$ Hz), 4.52 (bs, 1H, $N\underline{H}NHTos$), 7.04 (bs, 1H, $NHN\underline{H}Tos$), 7.2–8.0 (m, 4H, H_{arom})
b	CH_3	C_2H_5	76	129°	$C_{13}H_{23}N_2O_5PS$ (350.4)	0.86 (t, 3H, $PCCH_2C\underline{H}_3$, $J = 0.8$ Hz), 1.16 (d, 3H, $PCCH_3$, $J = 16$ Hz), 1.0–1.2 (m, 2H, $PCC\underline{H}_2CH_3$), 2.41 (s, 3H, $C_6H_3C\underline{H}_3$), 3.81 (d, 6H, $P(OCH_3)_2$, $J = 11$ Hz), 6.68 (bs, 1H, $NHN\underline{H}Tos$), 7.2–8.0 (m, 4H, H_{arom})
c	CH_3	C_6H_5	75	162–163°	$C_{17}H_{23}N_2O_5PS$ (398.4)	1.63 (d, 3H, $PCCH_3$, $J = 16$ Hz), 2.46 (s, 3H, $C_6H_4C\underline{H}_3$), 3.56 (dd, 6H, $P(OCH_3)_2$, $J = 11$ Hz, 19 Hz), 6.27 (bs, 1H, $NHN\underline{H}Tos$), 7.42 (s, 5H, H_{arom}), 7.2–8.0 (m, 4H, H_{arom})
d	$-(CH_2)_5-$		71	136–137°	$C_{15}H_{25}N_2O_5PS$ (376.4)	1.2–2.0 (m, 10H, C_6H_{10}), 2.45 (s, 3H, $C_6H_4C\underline{H}_3$), 3.47 (bs, 1H, $N\underline{H}NHTos$), 3.77 (d, 6H, $P(OCH_3)_2$, $J = 11$ Hz), 6.60 (bs, 1H, $NHN\underline{H}Tos$), 7.3–8.1 (m, 4H, H_{arom})
e	H	C_6H_5	78	146–147°	$C_{16}H_{21}N_2O_5PS$ (384.4)	2.49 (s, 3H, $C_6H_4C\underline{H}_3$), 3.67 (dd, 6H, $P(OCH_3)_2$, $J = 11$ Hz, 21 Hz), 4.24 (s, 1H, $N\underline{H}NHTos$), 4.39 (d, 2H, PCH, $J = 21$ Hz), 7.01, 7.77 (s, s, 1H, $NHN\underline{H}Tos$), 7.52 (s, 5H, H_{arom}), 7.3–8.2 (m, 4H, H_{arom})

[a] All products gave satisfactory microanalyses (C ± 0.1%, H ± 0,21%, N ± 0.26%).

Table 2. Dimethyl *sec*-Alkanephosphonates (**3**):

Compound **3**	R^1	R^2	Yield [%]	b.p./torr	Molecular formula[a]	^{1}H-N.M.R. Spectra ($CDCl_3$) δ [ppm]
a	CH_3	CH_3	71	60–62°/25	$C_5H_{13}O_3P$ (152.1)	1.05, 1.35 (d, 6H, $PC(CH_3)_2$), 1.6–2.4 (m, 1H, PCH), 3.76 (d, 6H, $P(OCH_3)_2$, $J = 11$ Hz)
b	CH_3	C_2H_5	75	70–72°/22	$C_6H_{15}O_3P$ (166.2)	0.8–2.4 (m, 9H, $PC\underline{H}(C\underline{H}_3)C_2\underline{H}_5$), 3.82 (d, 6H, $P(OCH_3)_2$, $J = 11$ Hz)
c	CH_3	C_6H_5	80	150–152°/2	$C_{10}H_{15}O_3P$ (214.2)	1.4–1.9 (m, 1H, PCH), 1.58 (d, 3H, $PCCH_3$, $J = 7$ Hz), 3.42 (dd, 6H, $P(OCH_3)_2$, $J = 8$ Hz, 10 Hz)
d	$-(CH_2)_5-$		50	100–102°/3	$C_8H_{17}O_3P$ (192.2)	1.2–2.4 (m, 11H, $PCHC_6H_{10}$), 3.68 (d, 6H, $P(OCH_3)_2$, $J = 10$ Hz)
e	H	C_6H_5	84	168–170°/25	$C_9H_{13}O_3P$ (200.2)	3.19 (d, 2H, PCH_2, $J = 13$ Hz), 3.62 (d, 6H, $P(OCH_3)_2$, $J = 10$ Hz), 7.32 (s, 5H, H_{arom})

[a] All products gave satisfactory microanalyses (C ± 0.1%, H ± 0.21%, N ± 0.26%).

aqueous hydrochloric acid, sodium hydrogen carbonate, and water; dried over sodium sulfate, and distilled under reduced pressure to give **3** (see Table 2).

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[1] W. Bamford, T. S. Stevens, *J. Chem. Soc.* **1952**, 4735.
[2] L. Caglioti, *Tetrahedron* **22**, 487 (1966).

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