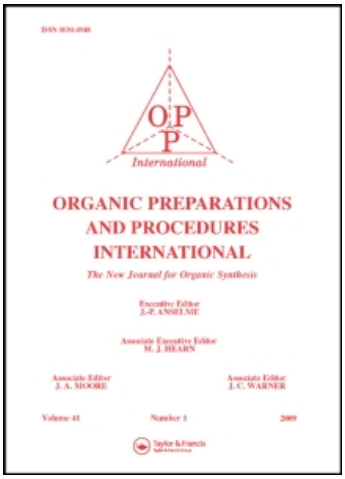

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

DI-ISOPROPYLPHOSPHINODITHIOIC ACID

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To cite this Article Corbin, James L. , Newton, William E. and McDonald, John W.(1975) 'DI-ISOPROPYLPHOSPHINODITHIOIC ACID', Organic Preparations and Procedures International, 7: 6, 309 — 310
To link to this Article: DOI: 10.1080/00304947509355167
URL: http://dx.doi.org/10.1080/00304947509355167

DI-ISOPROPYLPHOSPHINODITHIOIC ACID

Submitted by (8/21/75)

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We have reported[1] some novel chemistry of molybdenum complexes containing the di-isopropylphosphinodithioate ligand, and now give the details of its synthesis by a route that we found to be most expeditious.

The title compound has been reported as a by-product from the reaction of readily available $PSCl_3$ with i-PrMgBr, the main product being i-Pr_2PSCl. This suggested that the most direct route would be to treat the crude Grignard reaction

$$Cl_3P{=}S + \text{i-PrMgBr} \longrightarrow \text{i-}Pr_2P(S)Cl \xrightarrow{NaHS} \text{i-}Pr_2\text{-}P(S)SNa$$

product with NaSH. Thus the entire synthesis would involve only two steps and avoid the isolation of an intermediate. This approach gave i-Pr_2PS_2H in overall yields of 42-45%.

EXPERIMENTAL

Di-isopropylphosphinodithioic Acid. - An argon blanket was maintained where feasible during the entire synthetic sequence, gloves were worn and all manipulations were performed in a fume hood. The Gridnard reaction was run according to the literature procedure.[2]

The crude oil which was obtained after neutralization and the removal of solvent was dissolved in 150 ml of methanol and added to an NaSH solution (prepared by dissolving sodium (12.1 g) in methanol (150 ml), followed by saturation with H_2S). The resulting solution was refluxed for 5 hrs, cooled, the sodium chloride was filtered, and the solvent was removed (rotary evaporator). The residue was dissolved in 200 ml of water, was washed with benzene (2 x 75 ml), was then cooled in ice and was acidified with conc. HCl (50 ml). The oily product was extracted into benzene (2 x 75 ml), was washed with water (2 x 50 ml) and was dried (Na_2SO_4). After removing the solvent (rotary evaporator), the residual oil was distilled (vacuum-jacketed Vigreux column) under vacuum[3] to give 38-41 g of colorless i-Pr_2PS_2H (92-94°/0.02 mm).

Nmr ($CDCl_3$, 35°): The CH_3 protons resonated at 1.08, 1.19, 1.42, and 1.53 ppm, J_{PCCH} = 20 Hz and J_{HCCH} = 6.4 Hz. Other peaks were at 2.3 (m, CH) and 2.19 ppm (s, SH).

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*To whom correspondence should be addressed.

#Contribution No. 551.

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2. P. J. Christen, L. M. van der Linde and F. N. Hooge, Rec. Trav. Chim. Pays-Bos., 78, 161 (1959).

3. The presence of some very low-boiling material, including H_2S, required both liquid nitrogen and Dry-Ice/acetone traps to protect the pump.