

Syntheses of Some Thiolacetic Acid Derivatives¹

II. Phenyl- and 1-Naphthylthiolacetic Acids

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Phenylacetic acid has earlier been prepared by Johnson² from phenylacetyl chloride and a water solution of potassium hydrosulfide. Johnson describes the acid as an oil but gives no physical data. Sakurada³ reports the synthesis of phenylthiolacetic acid from the O-ethyl ester of the phenylthiolacetic acid through hydrolysis with an alcoholic solution of potassium hydroxide. Sakurada, however, describes the acid as yellow crystals, which definitely must be wrong (see below). 1-Naphthylthiolacetic acid does not seem to have been prepared before.

In our investigation of the plant growth activity of some thiolacetic acids^{4,5} these two acids seemed to be of interest and therefore were prepared. Phenyl- and 1-naphthylacetic acids were transformed to the corresponding acetyl chlorides by phosphorus pentachloride in carbon tetrachloride solution. The acid chlorides were thoroughly purified by vacuum distillation and then reacted with sodium hydrosulfide in water solution. Both thiolacetic acids were purified by vacuum distillation and the 1-naphthylthiolacetic acid was recrystallized as well. The physical data for the acetyl chlorides and the thiolacetic acids are given in Table 1.

The infra-red spectra of the phenylthiolacetic acid in a solution of carbon disulfide (Fig. 1) and of the 1-naphthylthiolacetic acid in KBr (Fig. 2) have been recorded.

Experimental results. Preparation of phenylacetyl chloride 45 g phenylacetic acid dissolved in 180 ml carbon tetrachloride was mixed with 70 g phosphorus pentachloride (equiv. amount) at 60°C. After completed reaction the carbon tetrachloride was distilled off. By vacuum distillation we obtained at 92–98°C and 7 mm Hg 40 g phenylacetyl chloride (yield 78 %). The product was redistilled at 90–92°C and 7 mm Hg. (Found: Cl 22.5. Calc. for C₈H₇OCl: Cl 22.9.)

Preparation of phenylthiolacetic acid. 31 g phenylacetyl chloride was slowly added to a sodium hydrosulfide solution (20 g sodium hydroxide dissolved in 150 ml water and saturated with hydrogen sulfide) at 70°C. After about an hour the reaction solution was cooled to room temperature and filtered. After acidifying with hydrochloric acid the precipitated oil was extracted with ether. The ether was dried with anhydrous sodium sulfate and distilled. At 90–93°C and 2 mm Hg we obtained 22 g phenylthiolacetic acid (59 %). The acid was further purified by distillation at 92°C and 2 mm Hg. (Found: S 20.9; equiv.wt. 151.0. Calc. for C₈H₈OS: S 21.06; equiv.wt. 152.22.)

Preparation of 1-naphthylacetyl chloride. 30 g 1-naphthylacetic acid (from PAL. Ltd, London, M. P. 132.3–132.7°C) dissolved in 110 ml carbon tetrachloride was reacted with 37 g phosphorus pentachloride as described above. At 152°C and 4 mm Hg 26 g 1-naphthylacetyl chloride was obtained (yield 79 %). (Found: Cl 18.1. Calc. for C₁₂H₉OCl: Cl 17.3.)

Preparation of 1-naphthylthiolacetic acid. 25 g 1-naphthylacetyl chloride was reacted with sodium hydrosulfide in the same way as phenylacetyl chloride. By acidifying after completed reaction a yellow oil was obtained, which was washed with water. By drying in vacuum the oil crystallized. The yield of crude 1-naphthylthiolacetic acid was 23 g (94 %). The acid was distilled in vacuum at 170–173°C and 1 mm Hg. Recrystallization from chloroform-petroleum ether gave light yellow crystals with m. p. 59.6–60.2°C. (Found: S 15.5; equiv.wt. 204.7. Calc. for C₁₂H₁₀OS: S 15.85; equiv.wt. 202.28.)

Table 1. Physical data.

Compound	Boiling point °C/mm Hg	Melting point °C	n_D^{20}	n_D^{20}	MR_D
Phenylacetyl chloride	90–92/7	colorless oil	1.5328	1.1697	141.00
Phenylthiolacetic acid	92/2	» »	1.5722	1.1409	43.91
1-Naphthylacetyl chloride	152/4	» »	1.6209	1.2281	58.60
1-Naphthylthiolacetic acid	170–173/1	59.6–60.2			

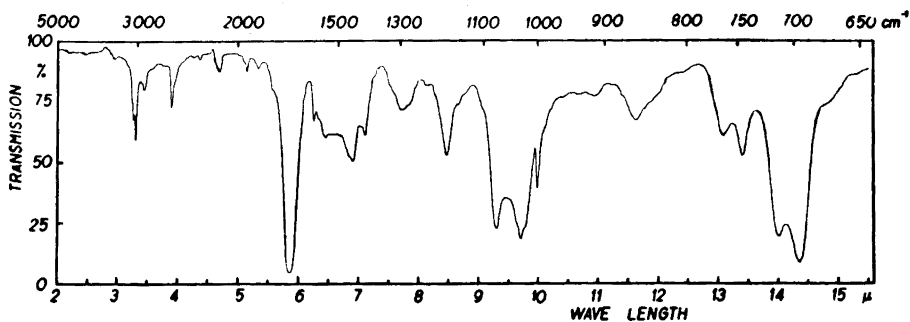


Fig. 1. The infra-red spectrum of phenylthiolacetic acid in CS_2 -solution.

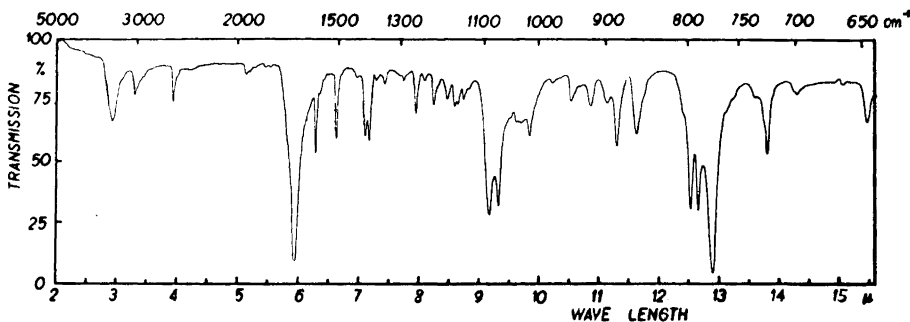


Fig. 2. The infra-red spectrum of 1-naphthylthiolacetic acid in KBr.

Infrared spectra were recorded with a Perkin-Elmer spectrometer, Model 21a, with a rock-salt prism. Slit schedule, corresponding to program 4. Speed 3 min/ μ . The frequencies of the absorption bands are given below in cm^{-1} .

Phenylthiolacetic acid (Fig. 1) 133.7 g/l CS_2 -solution. Cell: 0.1 mm 3 035 (w), 2 574 (w), 1 708 (s), 1 601 (w), 1 409 (m), 1 300 (w), 1 180 (m), 1 075 (s), 1 030 (s), 1 003 (m), 860 (m), 764 (m), 745 (m), 714 (s), and 697 (s).

1-Naphthylthiolacetic acid (Fig. 2) 2.0 mg/0.35 g KBr. 3 431 (w), 3 044 (w), 2 554 (w), 1 685 (s), 1 596 (w), 1 512 (w), 1 411 (w), 1 398 (w), 1 260 (w), 1 091 (m), 1 075 (m), 1 017 (w), 886 (w), 861 (w), 798 (m), 791 (m), 776 (s), 725 (w) and 648 (w).

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