Dinitrophenylhydrazones of Acetaldol and Dialdane

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In connection with a study of the degradation of potassium sorbate, it was necessary to prepare standard 2, 4-dinitrophenylhydrazones (DNPHs) of several aldehydes. This paper will report on the DNPHs of acetaldol and dialdane in the pure form.

There have been several articles[1-3] on acetaldol DNPH. The preparation of the hydrazone must be carried out in a neutral medium and, if possible, at room temperature; if not, crotonaldehyde DNPH is always produced. It has been reported that the melting point of Ross's hydrazone is 105°C, that of Pummerer *et al.*'s, 93—95°C, and that of Matthiessen's, 194.5°C. Undoubtedly, the last may be considered to be the melting point of crotonaldehyde DNPH, judging from its value and from its preparation in an acidic medium.

The present author prepared this hydrazone by refluxing a methanol solution of freshly-distilled acetaldol and 2, 4-dinitrophenylhydrazine for several hours. The crystalline powder thus obtained, mp 92—105°C, was repeatedly recrystallized from 50% methanol to afford yellow leaflets, mp 111.5—113°C. The thin-layer chromatography (TLC) of this material showed two spots, probably attributable to syn- and anti-isomers.[4,5] Thus the hydrazone could not be obtained in the pure form by recrystallization from 50% methanol. Purification by silica-gel chromatography, followed by recrystallization from chloroform, gave the hydrazone in the pure form as yellow needles, mp 113—114°C; its TLC showed a single spot, but this was not assigned to the alternative isomer. After being heated for a short time in 50% methanol, this sample showed two spots upon TLC. This suggested the probable formation of an equilibrium mixture during the recrystallization from 50% methanol. There has been no description of the recrystallization solvent of Ross's hydrazone, but Pummerer *et al.* recrystallized their hydrazone six times from aqueous ethanol. Therefore, it may be considered that the low melting point reported by Pummerer *et al.* is to be refered to an equilibrium mixture, although there are two additional possibilities, polymorphism and geometric isomerism.

The same behavior as that in the case of acetaldol DNPH was observed in the preparation of the DNPH of dialdane, a condensation product of acetaldol. In both cases, an attempt to isolate each fast-moving isomer by preparative TLC was unsuccessful.

Experimental[*1]

Acetaldol 2, 4-Dinitrophenylhydrazone. A mixture of 113.5 mg of freshly-distilled acetaldol, 261 mg of 2, 4-dinitrophenylhydrazine, and 30 m*l* of methanol was refluxed for several hours on a water bath. After the removal of the solvent under reduced pressure, the residual resinous matter was treated with ether. Then the unchanged hydrazine was separated, and the filtrate was again evaporated under reduced pressure to dryness. When the residue was treated with ether, a yellow powder separated, mp 92—105°C. This powder was repeatedly recrystallized from 50% methanol to afford yellow leaflets, mp 111.5—113°C; its TLC showed two spots, as a minor, fast-moving spot partly overlapped a major one. Then this material was chromatographed on a silica-gel column, using *n*-hexane-ethyl acetate (7 : 3) for development. The main band of the column was taken out and extracted with chloroform. The crystals from the extract were recrystallized from chloroform to afford yellow needles, mp 113—114°C; its TLC showed a single spot, R_f 0.14—0.15 in *n*-hexane-ethyl acetate (7 : 3) and R_f

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[1] J. H. Ross, *Anal. Chem.*, **25**, 1288 (1953).
[2] R. Pummerer, F. Aldebert, A. Büttner, F. Graser, E. Pirson, H. Rick and H. Sperber, *Ann.*, **583**, 161 (1953).
[3] G. Matthiessen, *Arch. Pharm.*, **284**, 62 (1951).
[4] G. A. Byrne, *J. Chromatog.*, **20**, 528 (1965).
[5] H. M. Edwards, Jr., *ibid.*, **22**, 29 (1966).

[*1] The melting points (capillary) are uncorrected. The microanalyses and the measurements of the infrared spectra were made by Mr. Jun'ichi Goda and his associates of Osaka City University, to whom the author is grateful. Thin-layer chromatography was performed on a plate with a 250 μ layer of silica-gel G (Merck), activated for one hour at 100°C. Each sample was dissolved in chloroform for placing it on the plate and developed over a 10 cm-long solvent path.

0.61—0.62 in benzene-tetrahydrofuran (7 : 3).*[2] The infrared spectrum is almost identical with that obtained by Ross, although the latter lacks the curve below 6 μ.

Found: C, 44.75, 44.90; H, 4.52, 4.36; N, 20.81, 20.73%. Calcd for $C_{10}H_{12}O_5N_4$: C. 44.77; H, 4.51; N, 20.89.%

Dialdane 2, 4-Dinitrophenylhydrazone. Crude dialdane was prepared according to the method described by Späth *et al.*[6] The corresponding hydrazone was prepared by stirring a solution of the crude dialdane and 2, 4-dinitrophenylhydrazine in 2 N hydrochloric acid at room temperature. The resulting precipitate had a mp of 150—153°C after being sintered at 80°C. Repeated recrystallizations from 50% methanol could not raise the melting point over 155°C; its TLC showed several spots. Purification by silica-gel chromatography, followed by recrystallization from chloroform, as in the case of acetaldol DNPH, gave the hydrazone in a pure form as yellow needles, mp 180°C (lit.[2] 173—174°C); its TLC showed a single spot, R_f 0.15 in *n*-hexane - ethyl acetate (7 : 3) and R_f 0.63—0.64 in benzene-tetrahydrofuran (7 : 3).

Found: C, 49.34, 49.44; H, 5.31, 5.58; N, 16.44%. Calcd for $C_{14}H_{18}O_6N_4$: C, 49.69; H, 5.36; N, 16.56%.

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*[2] Formaldehyde DNPH: R_f 0.58—0.59 and R_f 0.86—0.87 respectively in the same solvent systems.

[6] E. Späth, R. Lorenz and E. Freund, *Ber.*, **76B**, 722 (1943).