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2,4-Dinitrophenylhydrazones of Benzoin

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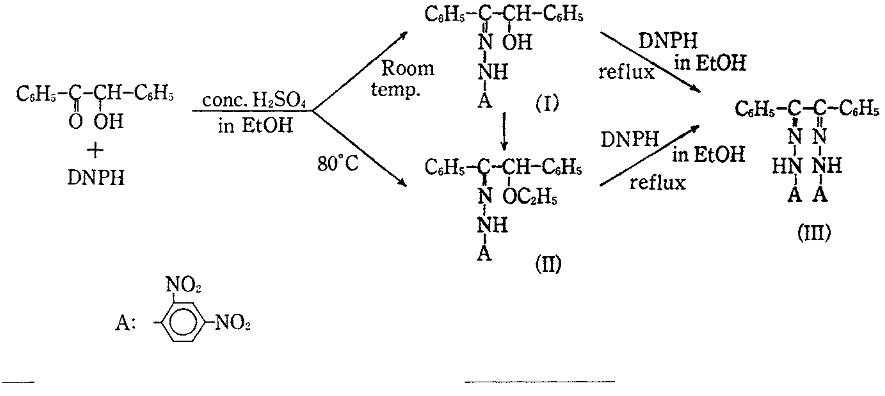
It is well known that the melting point of the 2,4-dinitrophenylhydrazone (DNP) of benzoin is 234°C.[1] Braude and Jones reported another DNP obtained from benzoin which melted at 174°C.[2] However, they stated nothing about the difference between the two.

Benzoin reacted with 2,4-dinitrophenylhydrazine (DNPH) prepared according to the procedure of Shriner and Fuson[3] at room temperature to give the DNP (I) (mp 236°C). On the other hand, when the reaction was carried out at 80°C for 45 min, the DNP (II) (mp 175°C), which is probably identical with that reported by Braude[2], was isolated as the main product. When the reaction was carried out at a temperature under 80°C, both I and II were formed. The I hydrazone was much more soluble in alcohol than II. The R_f values of I and II on the thin-layer chromatography using benzene-ether (17 : 3) were 0.74 and 0.94 respectively. When the reaction of benzoin and DNPH prepared according to Shriner's method was carried out under refluxing for 2 hr, di-DNP (osazone) of benzoin III, mp 314°C,[4] was obtained. III was also obtained when I or II was treated with Shriner's reagent at the boiling point. Further, I was converted to II when I was warmed at 80°C in ethanolic sulfuric acid.

The structure of II was confirmed as that of the DNP of benzoin ethyl ether on the basis of its elemental and spectral evidence; an absorption band as 1060 cm^{-1} in the infrared spectrum and signals at 8.60 (triplet, 3H, CH_3) and 6.15 τ (quartet, 2H, CH_2) in the NMR spectrum indicate the presence of an ethoxy group in II. Thus, it may reasonably be concluded that the hydroxy group of benzoin may be replaced by the ethoxy group in the reaction with DNPH in a hot alcoholic sulfuric acid solution. As acetoin and propionoin reacted with DNPH to form only sole DNP, even at 80°C, such behavior of benzoin seems somewhat peculiar.

Experimental[5]

Reaction of Benzoin with DNPH. *i) At Room Temperature.* Benzoin (3.5 g, 0.0165 mol) in 10 m*l* of ethanol was stirred into a solution of 18.5 g (0.09 mol) of DNPH in 150 m*l* of ethanol, 140 m*l* of water, and 92.5 m*l* of concentrated sulfuric acid. A nitrogen stream was then bubbled through the mixture. The precipitated product was filtered, washed with alcohol, and recrystallized from ethanol-ethyl acetate (3 : 1).



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[1] "Dictionary of Organic Compounds," ed. by J. R. A. Pollock and R. Stevens, 4th Ed., Eyre and Spottiswoode, Britain (1965), p. 344.

[2] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, **1945**, 501.

[3] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley & Sons, New York, N. Y. (1935), p. 148.

[4] Mp 317°C in Ref. 1, p. 334.

[5] All the melting points were determined on a Mettler electric micromelting-point apparatus and are uncorrected. The infrared spectra (KBr) were recorded on a Hitachi Model EPI-S2 spectrophotometer. The NMR spectra were determined in $(CD_3)_2CO$ on a JEOL NMR spectrometer at 60 MHz, with tetramethylsilane as the internal standard.

Mp 236°C.

Found: C, 61.90; H, 4.35; N, 13.29%. Calcd for $C_{20}H_{16}O_5N_4$: C, 61.22; H, 4.11; N, 14.28%.

ii) At 80°C. After the reaction mixture (the molar ratios were the same as those in the case of i) was heated at 80°C for 45 min, the solution was cooled. The precipitated product was filtered and then washed with ethanol. Recrystallization from ethanol-ethyl acetate (3 : 1) gave red-yellow crystals; mp 175°C.

Found: C, 63.13; H, 5.03; N, 12.72%. Calcd for $C_{22}H_{20}O_5N_4$: C, 62.85; H, 4.79; N, 13.33%.

Conversion of I to II. A few drops of conc. sulfuric acid were added to a solution of I (0.3 g) in 50 m*l* of ethanol. This solution was heated at 80°C for 2 hr. After cooling, the ethanol was evaporated under reduced pressure and the crude product was washed with ethanol. This reaction product indicated two spots on thin-layer chromatography; its R_f values were 0.72 and 0.94, identical with those of I and II.

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