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PREPARATION, SPECTROSCOPIC AND ACIDITY PROPERTIES OF TWO HYDRAZONES: AN ORGANIC LAB EXPERIMENT

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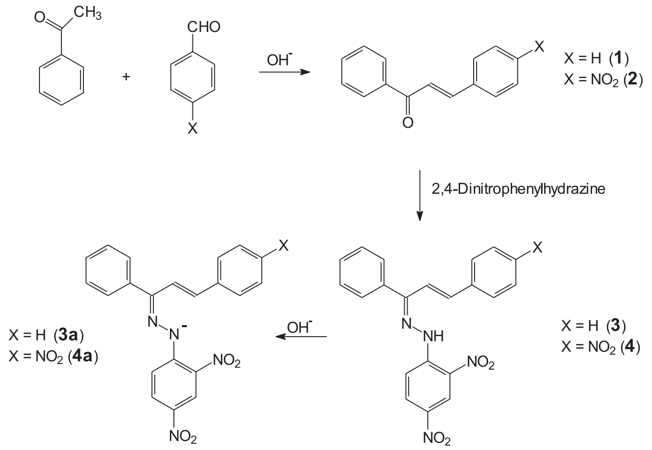
An undergraduate organic lab experiment is described based on the preparation of two readily accessible hydrazones. The UV-visible spectra of these N-H acids and of their conjugate bases are employed to illustrate the importance of through-conjugation in determining their acid strength and their internal charge-transfer-band transitions.

Keywords: polynitrophenylhydrazones; charge-transfer bands; acid-base indicators.

INTRODUCTION

Undergraduate students are familiar with the use of acid-base indicators, and of their colour changes at specific pH values. However, they are normally not encouraged to compare related indicators and rationalize their acid strength in structural terms. They are also more familiar with O-H acids, like carboxylic acids and phenols, and tend to overlook the fact that any hydrogen atom in an organic molecule may exhibit acidic properties, depending on its environment. In the present communication we describe a simple two-step preparation of two related hydrazones, which behave as indicators in basic medium. By comparing the properties of these two N-H acids with their structures, students may widen their view of the acid behaviour of organic compounds and of the influence of the molecular environment on the acidity of a particular proton.

Hydrazones **3** and **4**, prepared from diarylpropenones **1** and **2**, respectively, generate the corresponding anions **3a** and **4a**, by treatment with base.



This reaction is readily perceived by a colour change of the yellow solutions of these acids. Upon addition of drops of aqueous NaOH, methanolic solutions of **3** become pink, and solutions of **4** violet. Anions **3a** and **4a** differ in the number of nitro groups conjugated with the negatively charged nitrogen atom. As a result, these anions absorb at different wavelengths and also exhibit different stabilities. The presence of three nitro groups renders hydrazone **4** more acidic than **3**. This may be established by determination of the pKa values of the two hydrazones.

EXPERIMENTAL

Melting points were obtained with a capillary Microthermal instrument and were not corrected. IR spectra were recorded with a Perkin Elmer 750 equipment, ^{1}H-NMR spectra with a Bruker 400 Avance instrument. UV-visible spectra were recorded with a Bausch-Lomb TU-1800 spectrophotometer. Titrations were carried out with a HI 9321 Hanna pH-meter.

Benzaldehyde, acetophenone and 4-nitrobenzaldehyde were purchased from Aldrich and used without further purification.

1,3-diphenylpropenone (“benzylideneacetophenone” or “chalcone”) (1)

It was prepared by basic aldol condensation of benzaldehyde and acetophenone, following a reported procedure[1]. (Caution: Compound **1** is irritant. Contact with skin and eyes should be avoided)

Preparation of the 1-phenyl-3-(4-nitrophenyl)propenone (“4-benzylideneacetophenone”, “4-nitrochalcone”) (2)

The procedure below was adapted from the reported preparation of 1,3-diphenylpropenone[1]: to a cooled (5-10 °C) solution of NaOH (0.22 g, 5.5 mmol) in water (1 mL) and ethanol (2.2 mL) was added with stirring acetophenone (0.5 mL, 4.3 mmol) and a solution of 4-nitrobenzaldehyde (0.65 g, 4.3 mmol) in ethanol (20 mL). The resulting mixture was stirred for 3 h. The precipitated product was filtered, washed with water and dried to give 0.87 g (80% yield) of the 1-phenyl-3-(4-nitrophenyl)propenone, recrystallized from ethanol, mp 159-161 °C, lit. mp 158-160 °C [2].

In an alternative procedure[3], to a vigorously stirred, heated (*ca.* 100 °C) mixture of 4-nitrobenzaldehyde (0.76 g, 5 mmol) and acetophenone (0.72 g, 6 mmol) in 75 mL of water was added a solution of Na$_2$CO$_3$ (0.13 g, 1.25 mmol) in 25 mL water. The resulting mixture was allowed to react for 1 h. After cooling, the solid residue was filtered to give the 4-nitrobenzylideneacetophenone in 90% yield.

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Preparation of the 2,4-dinitrophenylhydrazone of 1,3-diphenylpropenone (3)

To a stirred, hot (50-60 °C) solution of 1,3-diphenylpropenone (0.1 g, 0.5 mmol) in methanol (3 mL) was added a hot (50-60 °C) acidic solution of 2,4-dinitrophenylhydrazine, prepared by careful addition of concentrated sulphuric acid (0.3 mL) to a suspension of 2,4-dinitrophenylhydrazine (0.12 g, 0.6 mmol) in methanol (5 mL). The hot mixture was stirred for 2 min and allowed to cool to 25 °C. The precipitated dinitrophenylhydrazone **4** was filtered and dried. The crude product weighed 0.18 g (93% yield) and was recrystallized from acetic acid., mp 244-246 °C, lit.[4] mp 248-249 °C. IR (KBr) 1613 (C=C), 1590, 1520 (NO_2), 1320 (NO_2), 1130, 740 and 690 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 6.56 (1 H, d, J = 16 Hz, C=C$\underline{H}$-Ar) ; 7.31-7.40 (6 H, m, phenyl H's *ortho* to C=N, *meta* and *para* to C=C, and C$\underline{H}$=C-Ar); 7.44-7.49 (2 H, d, J= 6.8 Hz, phenyl H's); 7.68-7.70 (3 H, m, phenyl H's *meta* and *para* to C=N); 8.12 (1 H, d, J= 9.8 Hz, H-6 of $C_6H_3(NO_2)_2$); 8.34 (1 H, dd, J= 9.8, J' = 2.5 Hz, H-5 of $C_6H_3(NO_2)_2$); 9.06 (1 H, d, J= 2.6 Hz, H-3 of $C_6H_3(NO_2)_2$); 11.12 (1 H, s, N-H).

Preparation of the 2,4-dinitrophenylhydrazone of 1-phenyl-3-(4-nitrophenyl)propenone (4)

To a stirred, boiling solution of 1-phenyl-3-(4-nitrophenyl) propenone (0.08 g, 0.32 mmol) in methanol (15 mL) was added a hot (50-60 °C) acidic solution of 2,4-dinitrophenylhydrazine, prepared by careful addition of concentrated sulphuric acid (0.5 mL) to a suspension of 2,4-dinitrophenylhydrazine (0.07 g, 0.36 mmol) in methanol (5 mL). The hot mixture was stirred for 5 min and allowed to cool to 25 °C. The precipitated dinitrophenylhydrazone **4** was filtered and dried. The crude product weighed 0.13 g (94 % yield) and was recrystallized from acetic acid, mp 268-270 °C, lit.[5] mp 259-259.5 °C. IR (KBr) 1614 (C=C), 1590, 1515 (NO_2), 1330 (NO_2), 1130, 840, 740 and 690 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 6.59 (1 H, d, J = 16.4 Hz, C=C$\underline{H}$-Ar); 7.34-7.37 (2 H, m, phenyl H's *ortho* to C=N); 7.42 (1 H, d, J = 16.4 Hz, C$\underline{H}$=C-Ar); 7.59 (2 H, d, J = 8.8 Hz, H's *meta* to O_2N-C_6H_4); 7.68-7.71 (3 H, m, phenyl H's *meta* and *para* to C=N); 8.14 (1 H, d, J= 9.6 Hz, H-6 of $C_6H_3(NO_2)_2$); 8.21 (2 H, d, J= 8.8 Hz, H's *ortho* to O_2N-C_6H_4); 8.37 (1 H, dd, J= 9.6, J' = 2.8 Hz, H-5 of $C_6H_3(NO_2)_2$); 9.07 (1 H, d, J= 2.8 Hz, H-3 of $C_6H_3(NO_2)_2$); 11.18 (1 H, s, N-H).

Acid-base measurements

Due to the poor solubility of hydrazones **3** and **4** in water, methanolic solutions (c = 2.5 x 10^{-5} M) were employed in all subsequent experiments. Their UV-visible spectra exhibited λ_{max} values at 390 and 395 nm respectively. Upon treatment with drops of hydroxide solution, the corresponding conjugate bases absorbed at 497 and 550 nm, respectively (Figure 1).

The acidity of compounds **3** and **4** was compared by the determination of their pKa values in methanol. To 30 mL of a stirred 2.5 x 10^{-5} M solution of the hydrazone was added with a microsyringe 10 µL of a 6 M aqueous NaOH solution. The pH of the solution was measured after each addition. UV-visible spectra of aliquots (3 mL) of this solution were recorded, and absorbance values read at 497 and 550 nm for compounds **3** and **4**, respectively. After each measurement the cuvette contents were returned to the mother solution.

Graphic treatment of the data with the aid of a plotting program (Origin) allowed the determination of the pKa values of compounds **3** and **4**. By plotting their absorbance readings at different pH values, sigmoid curves were obtained and their corresponding inflection points automatically determined, yielding pKa values of 12.3 for compound **3** (Figure 2) and 11.2 for compound **4** (Figure 3).

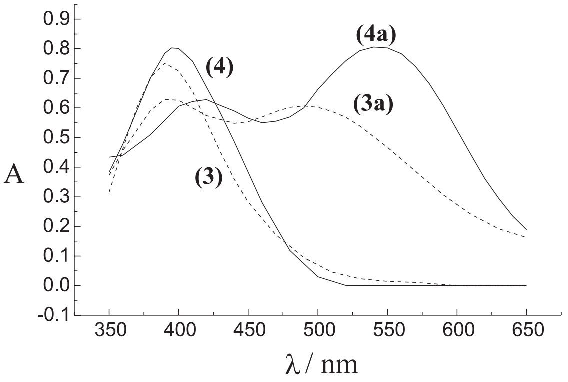


Figure 1. *UV-visible spectra of hydrazones **3** (dotted) and **4** (solid line) , and of their conjugate bases **3a** and **4a** in methanol* (ca *2.5 x 10*$^{-5}$ *M*)

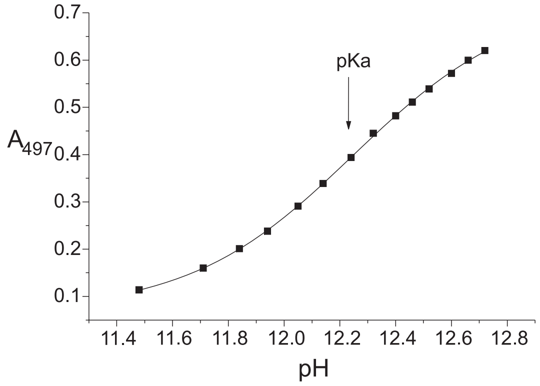


Figure 2. *Determination of hydrazone **3** pKa in methanol*

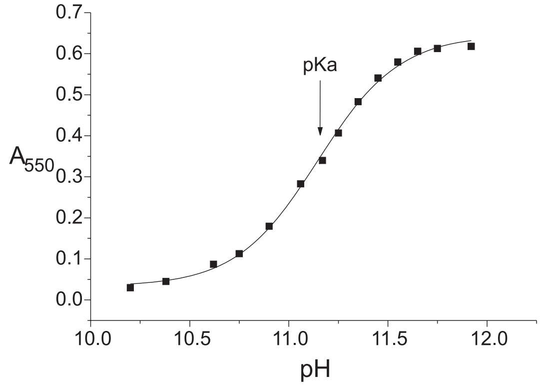
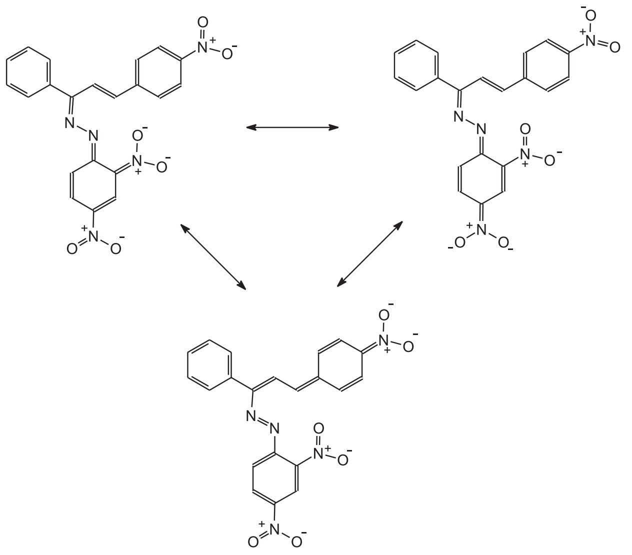


Figure 3. *Determination of hydrazone **4** pKa in methanol*

DISCUSSION

The preparation of the two indicators involves classic reactions of carbonyl compounds and may be used in a purely synthetic experiment. The preparation of chalcones **1** and **2** illustrates base-catalyzed aldol condensations of an aldehyde with a ketone possessing an acidic methyl group. The resulting α,β-unsaturated ketones undergo nucleophilic attack by 2,4-dinitrophenylhydrazine, a classic transformation employed for the characterization of ketones.

An analysis of the UV-visible spectra of compounds **3** and **4** and of their conjugate bases **3a** and **4a** will allow the instructor to discuss the influence of conjugation of donor and acceptor groups on the charge-transfer-band absorption of these molecules. Methanolic



(**4a**)

solutions of both acids absorb at nearly the same λ_{max} values. By contrast, the λ_{max} values of the internal charge-transfer bands of their conjugate bases differ by almost 50 nm (Figure 1) Students may be asked to rationalize the relative positions of these bands as the conjugation with a third NO_2 group shifts bathochromically the charge-transfer band of anion **4a** relative to anion **3a**. Students should be made aware that the effect of conjugation of the acidic N-H group with the third nitro substituent of the benzylidene fragment of **4a** extends over several bonds in the molecule.

Conjugation with a third nitro group is also responsible for the greater stability of anion **4a**, and, therefore, for the greater acidity of hydrazone **4**, when compared with compound **3**. This difference in acidity should be evident from a comparison of the obtained pKa values of the two hydrazones (Figures 2 and 3).

In conclusion, the preparation and the comparison of the UV-visible spectra and the acidity properties of the two hydrazones described in this communication may be used as an organic lab experiment to convey various concepts to an undergraduate student. Discussion and interpretation of the experimental results will provide the student with a background for the preparation of classic derivatives of carbonyl compounds. Moreover, he will be able to associate structure and conjugation in related molecules with their spectral behaviour and with the concept of internal charge-transfer. By comparing the acidity of the two prepared hydrazones, he will be able to relate conjugation between the acidic N-H group and the different NO_2 substituents in the molecules with their acid strength. Finally this example will also show him that the acidity of any proton in an organic molecule is determined not only by its neighbouring atoms, but by the molecule as a whole, in cases where through-conjugation may extend over several bonds.

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