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Sydnones. Synthesis and Photochromic Behavior of 3-(3-Pyridyl)sydnone Derivatives and a 4-Alkenyl-3-phenylsydnone

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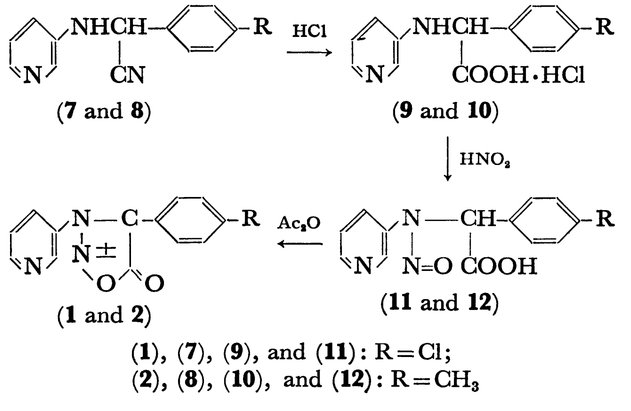
Six new sydnones [3-(3-pyridyl)-4-(*p*-chlorophenyl)sydnone (**1**), 3-(3-pyridyl)-4-(*p*-tolyl)sydnone (**2**), 3-(3-pyridyl)-4-(*p*-nitrophenyl)sydnone (**3**), 3-(3-pyridyl)-4-(*p*-aminophenyl)sydnone (**4**), 3-(3-pyridyl)-4-(*p*-acetamidophenyl)sydnone (**5**), and 3-phenyl-4-(α-phenylstyryl)sydnone (**6**)] were synthesized and examined for photochromic behavior. Sydnone **2** exhibited photochromism in the solid state upon UV irradiation (230—580 nm).

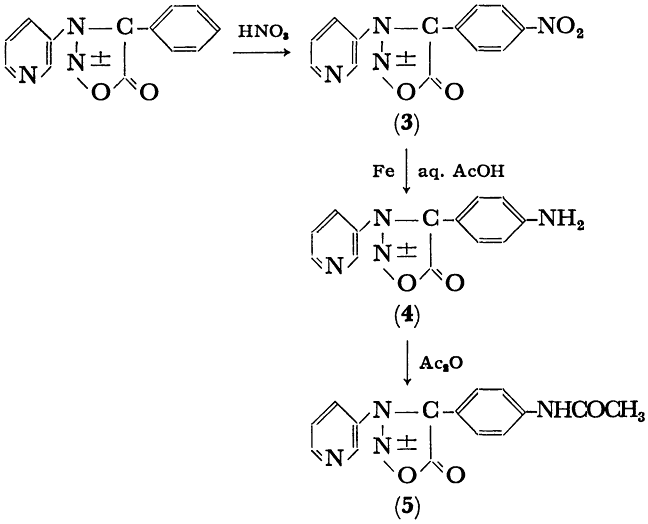
Photochromic 3-(3-pyridyl)sydnone was synthesized for the first time by Tien and Hunsberger. Later, several investigators prepared 3-(3-pyridyl)sydnone derivatives[1,2] and examined the effect of substituents on pyridylsydnone photochromism. However, none of the prepared sydnones exhibited photochromic behavior. Recently, several photochromic 4-alkenyl-3-phenylsydnones were synthesized by several groups[3–7] and investigated for photochromic properties. Here, the synthesis of new sydnones and their photochromic behavior is reported.

When *p*-chlorophenyl-(3-pyridylamino)acetonitrile (**7**) and *p*-tolyl-(3-pyridylamino)acetonitrile (**8**), which were easily obtained from the reaction of 3-aminopyridine with *p*-substituted benzaldehydes and potassium cyanide, were hydrolyzed with hydrochloric acid, *N*-(3-pyridyl)-*p*-chlorophenylglycine hydrochloride (**9**) and *N*-(3-pyridyl)-*p*-tolylglycine hydrochloride (**10**) were obtained. Compounds **9** and **10** easily reacted with sodium nitrite to afford *N*-nitroso-*N*-(3-pyridyl)-*p*-chlorophenylglycine (**11**) and *N*-nitroso-*N*-(3-pyridyl)-*p*-tolylglycine (**12**), which were then cyclized with acetic anhydride to give **1** and **2** in 50—70% yields.

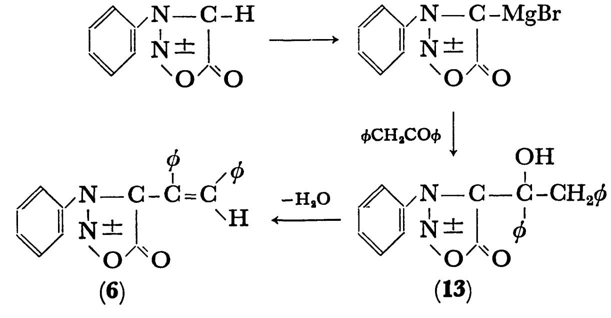


(**1**), (**7**), (**9**), and (**11**): R=Cl;
(**2**), (**8**), (**10**), and (**12**): R=CH_3

In order to obtain 4-(*p*-nitrophenyl)derivative **3**, the nitration of 3-(3-pyridyl)-4-phenylsydnone was examined. The nitration was accomplished in the following manner. Treatment of 3-(3-pyridyl)-4-phenylsydnone with fuming nitric acid at −5 °C afforded **3** in a moderate yield (52%). Compound **3** was readily reduced with iron powder in acetic acid at 90 °C to give 4-(*p*-aminophenyl)derivative **4** in a 45% yield. **4** underwent acetylation to give 4-(*p*-acetamidophenyl)-derivative **5** in an excellent yield (82%).



The reaction of 3-phenylsydnone with butylmagnesium bromide in THF at 2 °C gave the corresponding Grignard compound, which then reacted with deoxybenzoin to give 4-(1-hydroxy-1,2-diphenylethyl)-3-phenylsydnone (**13**) in a 54% yield. 3-Phenylsydnone derivative **13** was dehydrated by means of phosphoryl chloride and acetic anhydride to give 3-phenyl-4-(α-phenylstyryl)sydnone **6**, in an 88% yield.



The structures of the new sydnones (**1**—**6**) were assigned on the basis of their IR, NMR, mass, and UV spectra, and elemental analysis.

In the solid state, each of the new sydnones was exposed to ultraviolet radiation (230—580 nm). Sydnone **2** exhibited photochromism, with no other sydnones, however, exhibiting this behavior.

Sydnone **2** is a pale yellow compound, stable in air at room temperature if stored in the dark. **2** turned blue upon irradiation with ultraviolet light for a period of 3 to 5 min. This photochromic change was reversible; **2** returned to its original state after storage in the dark for several days. A more rapid recovery of **2** can be

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induced by heating at 80 °C for 30 min. After repeated exposures to ultraviolet radiation, **2** showed a delay in returning to its original state. The photochromic change was restricted to the crystalline state at room temperature; no such phenomenon was observed in solution.

An infrared spectrum of **2** was obtained and compared with that taken after a 5 min irradiation with ultraviolet light. The two spectra were essentially identical. The similarity between the infrared spectra of **2** before and after ultraviolet irradiation is an indication that there is no structural alternation associated with the photochromic change.

A conclusion drawn from these observations gives support to the proposition of Greco and O'Reilly[4] that the mesoionic ring may be a necessary, but not a sufficient, structural feature for photochromism. At present, the effect of molecular modification on the photochromism of compound **2** is being examined in order to elucidate the photochromic mechanism.

Finally, it should be noted that the new sydnones are comparatively stable even at high temperature.

Experimental

The IR spectra were recorded with a Hitachi Model 215 spectrophotometer and the UV spectra with a Hitachi Model EPS-3T spectrophotometer. The NMR spectra were obtained on a JEOL JNM-C-60H spectrometer, with tetramethylsilane as the internal reference. The mass spectra were determined on a Hitachi RMU-6E spectrometer. The melting points are uncorrected.

Materials. *p*-Chlorophenyl- and *p*-tolyl(3-pyridyl)acetonitriles (**7** and **8**) were prepared by the reaction of 3-aminopyridine with *p*-substituted benzaldehydes and potassium cyanide. **7**, mp 152—153 °C. Found: C, 64.12; H, 4.10; N, 17.21%. Calcd for $C_{13}H_{10}N_3Cl$: C, 64.07; H, 4.14; N, 17.24 %. **8**, mp 145.5—146.5 °C. Found: C, 75.30; H, 5.81; N, 18.77%. Calcd for $C_{14}H_{13}N_3$: C, 75.31; H, 5.87; N, 18.82%.

3-(3-Pyridyl)-4-phenylsydnone was prepared using the method of Ohta and Masaki.[1]

3-Phenylsydnone was also prepared by cyclization of *N*-nitroso-*N*-phenylglycine using the usual procedure.[8]

Hydrolysis of p-*Substituted Phenyl(3-pyridylamino)acetonitrile. Preparation of* N-*(3-Pyridyl)*-p-*chlorophenylglycine Hydrochloride(9) and* N-*(3-Pyridyl)*-p-*tolylglycine Hydrochloride (10)*: A mixture of **7** (2.0 g, 8 mmol) and concentrated HCl (18 ml) was stirred for 2 h under reflux. After cooling for 3 h at 0 °C, the resulting ammonium chloride was filtered, the solvent was distilled and the residue was heated with concentrated HCl for 15 min. After washing with concentrated HCl and recrystallization from concentrated HCl, pure **9** (2.1 g, 85%) was obtained.

The same procedure starting with acetonitrile (**8**) gave product **10** in a yield of 88%.

Glycine Hydrochloride (9), mp 223—227 °C. Found: C, 52.17; H, 4.01; N, 9.40%. Calcd for $C_{13}H_{12}N_2O_2Cl_2$: C, 52.19; H, 4.05; N, 9.37%.

Glycine Hydrochloride (10), mp 224—228 °C. Found: C, 60.34; H, 5.40; N, 9.99%. Calcd for $C_{14}H_{15}N_2O_2Cl$: C, 60.32; H, 5.43; N, 10.05%.

Nitrosation of Glycine Hydrochloride. Preparation of N-*Nitroso*-N-*(3-pyridyl)*-p-*chlorophenylglycine (11) and* N-*Nitroso*-N-*(3-pyridyl)*-p-*tolylglycine (12)*: To a suspension of **9** (4.4 g, 15 mmol) in water (45 ml) was added a 20% aqueous sodium hydroxide solution until compound **9** was completely dissolved. Sodium nitrite (1.2 g, 17 mmol) was added and concentrated HCl was then added at 0 °C until the solution showed acidity (pH 2) and then the reaction mixture was stirred for 30 min. After standing overnight at −2 °C, the deposited crystals were collected by filtration. Upon washing with cold water, pure **11** (3.4 g, 79%) was obtained.

Application of the same procedure to glycine hydrochloride (**10**) led to product **12** in a yield of 89%.

Nitrosoglycine (11), mp 140—141 °C (dec). Found: C, 53.51; H, 3.45; N, 14.42%. Calcd for $C_{13}H_{10}N_3O_3Cl$: C, 53.53; H,3.46; N, 14.41%.

Nitrosoglycine (12), mp 145.5—146.5 °C (dec). Found: C, 61.96; H, 4.82; N, 15.45%. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49%.

*3-(3-Pyridyl)-4-(*p*-chlorophenyl)sydnone (1).* A mixture of **11** (1.0 g, 3 mmol) and acetic anhydride (20 ml) was stirred for 2 h at room temperature. After heating for 5 min at 50 °C, the solvent was removed under reduced pressure in a nitrogen atmosphere. To the residual oil was added 50% ethanol and the mixture was then allowed to stand for a few minutes. The resulting crystals were filtered off and the residue was washed with ethanol and recrystallized from ethanol to give 0.6 g (64%) of sydnone **1** as pale yellow needles; mp 141—142 °C. IR (KBr): 1752 (C=O) and 1735 cm^{-1} (C=O); NMR ($CDCl_3$): δ 9.10—7.60 (4H, m, py) and 7.37 (4H, m, C_6H_4); UV (MeOH) max: 254 (ε 12400) and 340 nm (10500); MS *m/e* (%): 273 (M^+, 57), 215 (100), and 78 (58). Found: C, 57.25; H, 2.78; N, 15.13%. Calcd for $C_{13}H_8N_3O_2Cl$: C, 57.05; H, 2.95; N, 15.35%.

*3-(3-Pyridyl)-4-(*p*-tolyl)sydnone (2).* A mixture of **12** (1.0 g, 4 mmol) and acetic anhydride (10 ml) was stirred for 3 h at room temperature. After heating for 5 min at 70 °C, the mixture was worked up using the same method as described above to give 0.52 g (56%) of sydnone **2** as pale yellow needles; mp 142—143 °C. IR (KBr): 1745 cm^{-1} (C=O); NMR ($CDCl_3$): δ 9.05—7.50 (4H, m, py), 7.22 (4H, m, C_6H_4), and 2.64 (3H, s, CH_3); UV (MeOH) max: 251 (ε 7950) and 341 nm (6170); MS *m/e* (%): 253 (M^+, 60), 195 (100), and 78 (26). Found: C, 66.34; H, 4.17; N, 16.59%. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.37; N, 16.59%.

*3-(3-Pyridyl)-4-(*p*-nitrophenyl)sydnone (3).* To fuming nitric acid (10 ml) was slowly added 3-(3-pyridyl)-4-phenylsydnone (2.0 g, 8 mmol) at −5 °C which was then stirred for 20 min. The reaction mixture was poured into ice water. The resulting crystals were filtered off and washed several times with cold water and then crystallized from 60% ethanol to give 1.2 g (52%) of synone **3** as yellow needles; mp 162—163 °C. IR (KBr): 1770 (C=O), 1750 (C=O), 1520 (NO_2), 1353 (NO_2), and 856 cm^{-1}; NMR (DMSO-d_6): δ 9.10—7.84 (8H, m, py and C_6H_4); UV (MeOH) max: 262 (ε 7080) and 362 nm (17000); MS *m/e* (%): 284 (M^+, 63), 226 (100), 180 (38), and 78 (66). Found: C, 55.03; H, 2.67; N, 19.71%. Calcd for $C_{13}H_8N_4O_4$: C, 54.93; H, 2.83; N, 19.71%.

*3-(3-Pyridyl)-4-(*p*-aminophenyl)sydnone (4).* To a suspension of **3** (3.5 g, 12 mmol) in hot water were added iron powder (8 g) and acetic acid (10 ml) and then the mixture was stirred for 20 min at 95 °C. After cooling, the reaction mixture was neutralized with $NaHCO_3$. The precipitate was filtered and washed several times with cold water. After drying, the residue was extracted with THF (100 ml) three times, and then the solvent was concentrated under reduced pressure in a nitrogen atmosphere. Petroleum ether (40 ml) was added and the mixture was coold. The resulting crystals were collected by filtration and then washed with petroleum ether. Recrystallization from absolute ethanol afforded 1.4 g (45%) of pure **4** as pale yellow needles; mp 194.5—196 °C. IR (KBr): 3425 (NH_2), 3342 (NH_2), and 1735 cm^{-1} (C=O); NMR (py-d_5): δ

9.02—7.40 (4H, m, py), 7.36—6.65 (4H, m, C_6H_4), and 5.35 (2H, s, NH_2); UV (MeOH) max: 266 (ε 13200) and 378 nm (6760); MS *m/e* (%): 254 (M^+, 27) and 196 (100). Found: C, 61.28; H, 3.80; N, 21.96%. Calcd for $C_{13}H_{10}N_4O_2$: C, 61.41; H, 3.96; N, 22.04%.

*3-(3-Pyridyl)-4-(*p*-acetamidophenyl)sydnone (**5**).* A mixture of **4** (0.20 g, 0.78 mmol), acetic anhydride (1.5 ml), and acetic acid (5 ml) was stirred for 20 min at 80 °C. The solvent was removed under reduced pressure in a nitrogen atmosphere. To the residual oil ethanol (2 ml) was added. The resulting crystals were collected by filtration. Recrystallization from 50% ethanol afforded 0.19 g (82%) of pure **5** as yellow needles; mp 242—244 °C. IR (KBr): 3300 (NH), 1720 (C=O), and 1678 cm^{-1} ($CH_3C{=}O$); NMR (DMSO-d_6): δ 9.00—7.80 (4H, m, py), 7.75—7.15 (4H, m, C_6H_4), 3.56 (1H, s, NHC=O), and 3.15 (3H, s, $CH_3C{=}O$); UV (MeOH) max: 269 (ε 8710) and 351 nm (6760). Found: C, 60.82; H, 4.01; N, 18.88%. Calcd for $C_{15}H_{12}N_4O_3$: C, 60.80; H, 4.09; N, 18.91%.

*Grignard Reaction. Preparation of 4-(1-Hydroxy-1,2-diphenylethyl)-3-phenylsydnone (**13**)*: To butylmagnesium bromide (30 ml, 50 mmol)[9] was added a solution of 3-phenylsydnone (3.2 g, 20 mmol) in THF (80 ml) at 2—3 °C which was then stirred for 1 h. To this was added a solution of deoxybenzoin (10.0 g, 50 mmol) in THF (10 ml) at 5 °C and this mixture was then stirred for 2 h and poured into dilute acetic acid. The reaction mixture was extracted with benzene (100 ml) three times. The extract, after washing with water (50 ml) three times and drying over anhydrous magnesium sulfate, was concentrated in a nitrogen atmosphere. The residue was purified by washing with benzene–hexane (1: 1) to give **13** (3.8 g, 54%).

*Sydnone (**13**)*; mp 130—131 °C. Found: C, 73.65; H, 5.12; N, 7.84%. Calcd for $C_{22}H_{18}N_2O_3$: C, 73.72; H, 5.07; N, 7.81%.

*Dehydration of 4-(1-Hydroxy-1,2-diphenylethyl)-3-phenylsydnone. Preparation of 3-Phenyl-4-(α-phenylstyryl)sydnone (**6**)*: To a solution of **13** (0.5 g, 0.14 mmol) in pyridine (10 ml) was added phosphoryl chloride (2 ml) at −5 °C. After standing for 12h at room temperature, the mixture was heated for 2 h and then poured into ice water. The resulting crystals were collected by filtration. Recrystallization from 50% ethanol afforded 0.22 g (47%) of pure **6** as pale yellow needles; mp 172—174 °C. IR (KBr): 1735 (C=O) and 818 cm^{-1} (C=CHR); NMR ($CDCl_3$): δ 7.56—7.12 (15H, m, C_6H_5) and 6.32 (1H, s, CHR); UV (MeOH) max: 231 (ε 11220) and 351 nm (8320); MS *m/e* (%): 330 (M^+, 18) and 272 (100). Found: C, 77.60; H, 4.76; N, 8.20%. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23%.

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