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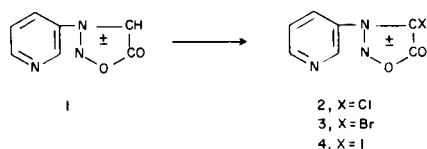
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Halogenation of 3-(3-pyridyl)sydnone with *N*-halosuccinimides in chloroform afforded the 4-halogeno-3-(3-pyridyl)sydnone where X = Cl, Br, I. The 4-chloro- and 4-bromopyridylsydnone were photochromic. 3-(3-Pyridyl)sydnone was obtained in both high yield and purity by dehydration of *N*-nitroso-*N*-(3-pyridyl)glycine with trifluoroacetic anhydride.

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Since the synthesis of 3-(3-pyridyl)sydnone (**1**) (3,4), 4-methyl and 4-phenyl analogs were synthesized (5a) as well as the 5-bromopyridyl and *N*-oxide analogs (6), none of which were photochromic. However, the 4-*p*-tolyl analog was recently reported (5b) to be photochromic.

Since our discovery of photochromism in 3-phenylsydnone substituted alkenes (7), we have continued our search for structural parameters responsible for photochromism in sydnone. We therefore undertook the synthesis of 4-halogeno-3-(3-pyridyl)sydnone (**2-4**) to determine the effect of this substitution on this property.



Various methods for the halogenation of sydnone at the four position have been reported (8). A chlorination reported (9) for 3-phenylsydnone employing *N*-chlorosuccinimide in methanol seemed an appropriate method for pyridylsydnone. Application successfully afforded 4-chloro-3-(3-pyridyl)sydnone (**2**).

Bromination of 3-phenylsydnone was achieved either by refluxing with *N*-bromosuccinimide in chloroform (10) or reaction with a mixture of bromine, ethanol and sodium bicarbonate (11). A bromination of **1** with bromine in acetic acid was described (12), but there was no mention of any photochromic behavior by **3**. We synthesized **3** in higher yield by reacting **1** with either *N*-bromosuccinimide in methanol or a mixture of bromine, aqueous ethanol, and sodium bicarbonate.

Iodination of 3-phenylsydnone had been accomplished indirectly from the 4-chloromercuri (13) or Grignard derivatives (14). The conversion of 4-chloromercuri-3-(3-pyridyl)sydnone (**3**) gave very impure 4-iodo-3-(3-pyridyl)sydnone (**4**), because of contamination by the 4-chloromercuri precursor. Direct iodination of **1** with *N*-iodosuccinimide in chloroform proved to be the most convenient method although several recrystallizations from benzene were necessary to remove succinimide.

We found trifluoroacetic anhydride, as reported in a

synthesis of 3-phenylsydnone (15), to be superior to acetic anhydride for the dehydration of *N*-nitroso-*N*-(3-pyridyl)glycine affording **1** in high yield and purity.

The ultraviolet spectral absorptions of the sydnone ring in compounds **2-4** underwent a gradual cumulative bathochromic shift relative to the absorption of **1** (312 nm). The shift was about 5 nm per halogen as the electro-negativity decreased and was accompanied for all halogens by an increase in intensity of absorption. The pyridine ring absorption of **1** (236 nm with a 265 nm shoulder) decreased in intensity in compounds **2-4** and was further altered by a bathochromic shift for compounds **3** and **4** with concomitant loss of the shoulder.

Only the halogenopyridylsydnone **2** and **3** were photochromic at both 254 nm and 366 nm wavelengths. The chloro-compound **2** exhibited a faint blue-green coloration while the bromo-compound **3** exhibited a navy-blue coloration at both short and long wavelengths of irradiation. Sometime after completion of this study (2) the photochromic behavior of **3** was described in detail (16). These workers observed the irreversibility of the color change in **3**. A strict definition of photochromism would exclude this compound and consider its behavior to be ordinary photochemistry.

EXPERIMENTAL (17)

3-(3-Pyridyl)Sydnone (**1**).

A fine suspension of *N*-nitroso-*N*-(3-pyridyl)glycine (4) (50 g., 0.28 mole) in absolute ether (350 ml.) at 0° was treated dropwise, with stirring, with trifluoroacetic anhydride (75 ml.) and the mixture was stirred an additional 1 hour at 0°. The crude product (40.8 g., 89.7%), m.p. 116-120°, was filtered and washed with absolute ether (3 x 50 ml.). Recrystallization from benzene afforded pure **1** (37.9 g., 83.3%), m.p. 119-120.5° (lit. (4) m.p. 119-121°). The infrared spectrum of this product was superimposable on one of an authentic sample; uv: λ max 236 nm (log ϵ 4.93), 265 sh (3.67), 312 (3.66); nmr: δ 9.36 (d, 1H, H₂, J_{2,4} = 2 Hz), 8.97 (pair d, 1H, H₆, J_{6,4} = 1 Hz, J_{6,5} = 5 Hz), 8.47 (pair quartets, 1H, H₄, J_{4,5} = 8 Hz), 7.83 (q, 1H, H₅), 7.93 (s, 1H, sydnone CH).

4-Chloro-3-(3-Pyridyl)sydnone (**2**).

A suspension of **1** (1.63 g., 0.01 mole) and *N*-chlorosuccinimide (1.99 g., 0.015 mole) in dry chloroform (75 ml.) was refluxed 0.5 hour, cooled, filtered, and the filtrate evaporated *in vacuo* to an oil which solidified. The crude solid was dissolved in boiling THF (125 ml.), filtered (residue discarded), and the filtrate evaporated *in vacuo* to give 1.2 g. (60%) of

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product. A recrystallization from absolute ether afforded pure product (0.9 g., 45%), m.p. 120-122°; ir: μ 5.60 and 5.70 (sydnone carbonyl), uv: λ max 235 nm ($\log \epsilon$ 3.76), 255 sh (3.69), 317 (3.84); nmr: δ 9.10 (d, 1H, H₂, J_{2,4} = 8 Hz), 9.01 (d, 1H, H₆), 8.42 (pair d, 1H, H₄, H_{4,6} = 8 Hz), 7.87 (q, 1H, H₃, J_{3,6} = 5 Hz).

Anal. Calcd. for C₇H₄ClN₃O₂: C, 42.55; H, 2.04; N, 21.27; Cl, 17.94. Found: C, 42.37; H, 2.17; N, 21.39; Cl, 18.08.

4-Bromo-3-(3-Pyridyl)sydnone (3).

(a) With *N*-Bromosuccinimide.

A solution of **1** (1.63 g., 0.01 mole) and NBS (1.96 g., 0.011 mole) in 95% methanol (100 ml.) was stirred for 5 minutes at room temperature, filtered, and the filtrate was evaporated to give a crude solid. This was dissolved in warm water (200 ml.), and hot methanol (20 ml.) was added to dissolve any residual solid. The cooled aqueous methanol was extracted with chloroform (2 x 100 ml.), dried (magnesium sulfate) filtered, and the filtrate was evaporated to yield 2.0 g. (82.6%) of product. An additional recrystallization from benzene yielded pure product (1.45 g., 59.9%), m.p. 134-136° (lit. (12) m.p. 136°).

(b) With Bromine.

At room temperature, sodium bicarbonate (6.8 g., 0.082 mole) in 120 ml. of water was added to a solution of **1** (3.26 g., 0.02 mole) in ethanol (150 ml.). This cloudy solution changed to a clear orange color on addition of bromine (3.6 g., 0.022 mole) in 25 ml. of ethanol. After stirring 45 minutes, water was added until the solution cleared. Overnight refrigeration yielded the product (2.13 g., 44%), m.p. 134-136°. A recrystallization from boiling benzene to which hexane was added to the cloud point afforded pure **3** (1.96 g., 40.5%), m.p. 135-136°; ir: μ 5.70 and 5.80 (sydnone carbonyl); uv: λ max 246 nm ($\log \epsilon$ 3.77), 322 (3.90); nmr: δ 9.08 (s, 1H, H₂), 9.00 (s, 1H, H₆), 8.42 (d, 1H, H₄), 7.87 (q, 1H, H₃).

Anal. Calcd. for C₇H₄BrN₃O₂: C, 34.73; H, 1.67; N, 17.36; Br, 33.02. Found: C, 34.95; H, 1.93; N, 17.11; Br, 33.29.

4-Iodo-3-(3-Pyridyl)sydnone (4).

This compound was prepared by the identical procedure described for **3**, method (a), except *N*-iodosuccinimide (2.48 g., 0.011 mole) was substituted for NBS. Pure product (0.65 g., 22.6%), m.p. 152-154°, was obtained after three recrystallizations from benzene; ir: μ 5.75 and 5.80 (sydnone carbonyl); uv: λ max 255 nm ($\log \epsilon$ 3.63), 327 (3.85); nmr: δ 9.03 (s, 1H, H₂), 8.95 (s, 1H, H₆), 8.33 (pair d, 1H, H₄), 7.80 (q, 1H, H₃).

Anal. Calcd. for C₇H₄I₂N₃O₂: C, 29.09; H, 1.40; N, 14.54; I, 43.91. Found: C, 29.23; H, 1.52; N, 14.81; I, 43.70.

REFERENCES AND NOTES

- (1) Part X., C. V. Greco and J. R. Mehta, *J. Chem. Soc., Perkin Trans. I*, in press.
- (2) Taken from the doctoral dissertation of J. R. Mehta, St. John's University, New York, N. Y., 1974.
- (3) J. M. Tien and I. M. Hunsberger, *J. Am. Chem. Soc.*, **83**, 178 (1961).
- (4) J. M. Tien and I. M. Hunsberger, *ibid.*, **77**, 6604 (1955).
- (5a) M. Ohta and M. Masuki, *Bull. Chem. Soc. Japan*, **33**, 649 (1960);
- (b) S. Inoue, N. Asai, G. Yasuda and T. Hori, *ibid.*, **50**, 3268 (1977).
- (6) C. V. Greco and I. M. Hunsberger, *J. Heterocyclic Chem.*, **7**, 761 (1970).
- (7) C. V. Greco and B. P. O'Reilly, *ibid.*, **9**, 207 (1972).
- (8) Consult M. Ohta and H. Kato, "Nonbenzenoid Aromatics", J. P. Snyder, Ed., Vol. 16-1, Academic Press, New York, N. Y., 1969, pp. 146-147.
- (9) B. V. Badami, Doctoral Thesis, Karnatak University, India, 1972.
- (10) H. Kato, K. Nakahara and M. Ohta, *Nippon Kagaku Zasshi*, **77**, 1304 (1955); *Chem. Abstr.*, **53**, 5250 (1959).
- (11) C. V. Greco, M. Pesce and J. M. Franco, *J. Heterocyclic Chem.*, **3**, 391 (1966).
- (12) G. S. Puranik and H. Suschitzky, *J. Chem. Soc., C*, 1006 (1967).
- (13) K. Nakahara and M. Ohta, *Nippon Kagaku Zasshi*, **77**, 1306 (1955); *Chem. Abstr.*, **54**, 1503 (1960).
- (14) M. Ohta and H. Kato, *ibid.*, **78**, 1653 (1957); *Chem. Abstr.*, **54**, 1503 (1960).
- (15) W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 1542 (1950).
- (16) S. Nespurek and M. Sorm, *Collect. Czech. Chem. Commun.*, **42**, 811 (1977).
- (17) All melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra (potassium bromide) were measured on a Perkin Elmer Infracord 137, ultraviolet spectra (in methanol) on a Cary Model 14 Spectrophotometer, and nuclear magnetic resonance spectra on a Varian A60A (DMSO-*d*₆) with TMS as the internal standard, chemical shifts reported in ppm (δ). Combustion analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Tests for photochromism were performed with a Blak-Ray UVL-22 (366 nm, 4 watts) manufactured by Ultraviolet Products, Inc., San Gabriel, California.