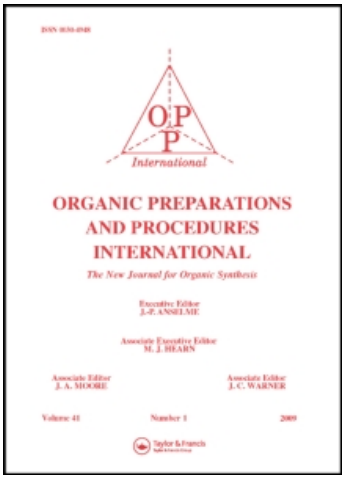


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN IMPROVED PROCEDURE FOR THE SYNTHESIS OF SALICYLALDEHYDE HYDRAZONE

Charles F. Hoyng[a]
[a] Department of Chemistry, Texas A & M University, College Station, Texas

To cite this Article Hoyng, Charles F.(1980) 'AN IMPROVED PROCEDURE FOR THE SYNTHESIS OF SALICYLALDEHYDE HYDRAZONE', Organic Preparations and Procedures International, 12: 3, 253 — 255
To link to this Article: DOI: 10.1080/00304948009458565
URL: http://dx.doi.org/10.1080/00304948009458565

The procedure described above gives 2-fluoro-1,4-naphthalenedione completely free from the 2-chloro compound, as evidenced by the ^1H nmr spectrum (total absence of the singlet at δ 7.16 due to the H-3 proton of 2-chloro-1,4-naphthalenedione). The modest yield is due to the formation of highly polar, coloured by-products.

In trial experiments, 2-bromo-1,4-naphthalenedione was found to be an inferior substitute for the chloro compound, substantial decomposition occuring under the conditions of the reaction. Several attempts were also made to perform the reaction at lower temperatures using a dipolar aprotic solvent, but only tarry mixtures were obtained.

The 2-fluoro-1,4-naphthalenedione prepared as described above was used to prepare a series of alkylated compounds, which were used in antifungal testing.[5]

REFERENCES

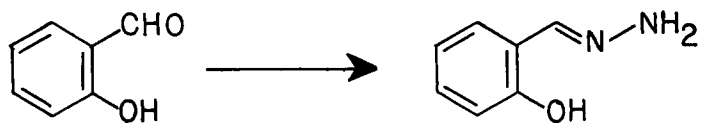
1. D. M. Fieldgate and D. Woodcock, Pestic. Sci., 4, 193 (1973).
2. L. S. Fosdick and J. C. Calandra, J. Dental Research, 26, 309 (1947).
3. P. H. H. Fischer and H. Zimmermann, Z. Naturforsch., A23, 1399 (1968).
4. L. F. Fieser, J. Am. Chem. Soc., 70, 3165 (1948).
5. C. S. James, R. S. T. Loeffler and D. Woodcock, Unpublished results.

AN IMPROVED PROCEDURE FOR THE SYNTHESIS OF SALICYLALDEHYDE HYDRAZONE

Submitted by Charles F. Hoyng
(3/24/8)
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Although hydrazones of aryl aldehydes with electron-rich aromatic ring systems are generally unstable compounds,[1] salicylaldehyde hydrazone

(II) is a stable, crystalline substance. This compound has previously been prepared in 20% yield by the action of hydrazine hydrate on 2-aldehydophenyl ethyl carbonate.[2] In addition, direct treatment of salicylaldehyde with hydrazine hydrate has been reported to yield II, but the reaction product was contaminated with small quantities of salicylaldehyde azine.[2] This impurity cannot be removed without loss of II. Even mild purification procedures, such as low temperature recrystallization, prove unsuccessful. The simplified synthetic procedure reported herein, allows the conversion of salicylaldehyde (I) into pure salicylaldehyde hydrazone (II) in 64% yield.



I II

The pmr spectrum indicated that salicylaldehyde hydrazone (II) exists as a single geometric isomer,[3] which was assigned that of the anti-isomer, II. The chemical shift of the phenolic -OH peak is characteristic of a strong intramolecular hydrogen bond, possible only in the anti-isomer.[4] This feature may be responsible for the observed geometric preference, and could also account for the observed stability of salicylaldehyde hydrazone.

EXPERIMENTAL

IR spectra were determined on a Perkin-Elmer Model 297 spectrometer, and pmr (^{1}H NMR) spectra were recorded with a Varian Model T-60 spectrometer. Chemical shifts are reported on solutions as δ values in ppm relative to TMS as an internal standard. The melting point is uncorrected.

Salicylaldehyde hydrazone (II).- A solution of 6.1 g (50 mmol) of salicylaldehyde (I) in 135 ml of absolute ethanol was added dropwise (40 min.) to a solution of 5.9 g (100 mmol) of 85% hydrazine hydrate in 10 ml of absolute ethanol. The colorless, homogeneous solution was chilled to -20° to

obtain a colorless, crystalline solid, salicylaldehyde hydrazone (II). The solid was collected, washed with a small portion of cold (0°) absolute ethanol, and air dried. The combined mother liquor and ethanol washing was concentrated to a volume of approximately 65 ml and chilled to -20°. A second crop of colorless, crystalline product was obtained. The two samples were combined to provide 4.3 g (64%) of salicylaldehyde hydrazone (II), mp 96-97°, lit.[2] 96°. IR ($CHCl_3$): 3400, 3100, 2990, 2910, 1620, 1570, 1490, 1390, 1265, 1150, 1030, 940, 900 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.48 (bs, 2H, =N-NH_2), 7.12 (m, 4H, aryl), 7.95 (s, 1H, -CH=N-), 11.14 (bs, 1H, -OH).

Acknowledgement.- Financial support from The Robert A. Welch Foundation is gratefully acknowledged.

REFERENCES

1. S. Patai, "The Chemistry of the Carbon-Nitrogen Double Bond," Interscience Publishers, New York, 1970, p. 71 and references therein.

2. H. Cajar, Ber., 31, 2803 (1898).

3. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, Oxford, 1969, p. 226 and references therein.

4. A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, J. Am. Chem. Soc., 82, 5057 (1960); L. W. Reeves, Can. J. Chem., 38, 748 (1960).

OXIDATION OF AMINO ALCOHOLS TO AMINO KETONES

Submitted by Robert E. Lyle*†, John R. Maloney and Roger J. White
(2/11/80)
Department of Chemistry
North Texas State University
Denton, TX 76203

The oxidation of amino alcohols to amino ketones is experimentally difficult since the bidentate functionality of the amino ketones frequently forms strong complexes with the metal cation of the oxidizing agent complicating the isolation; moreover, the amino ketone may be oxidized further