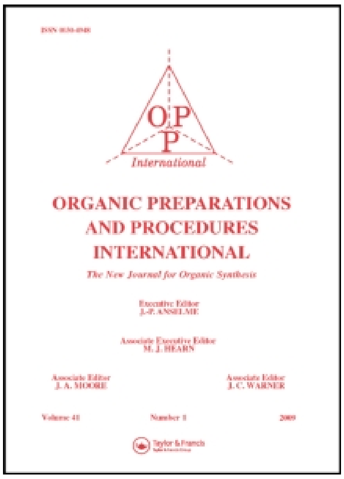


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

2-FLUORO-1,4-NAPHTHALENEDIONE

R. S. Thomas Loeffler[a]; Carolyn S. James[a]
[a] University of Bristol Long Ashton Research Station, Bristol, ENGLAND

To cite this Article Loeffler, R. S. Thomas and James, Carolyn S.(1980) '2-FLUORO-1,4-NAPHTHALENEDIONE', Organic Preparations and Procedures International, 12: 3, 251 — 253
To link to this Article: DOI: 10.1080/00304948009458564
URL: http://dx.doi.org/10.1080/00304948009458564

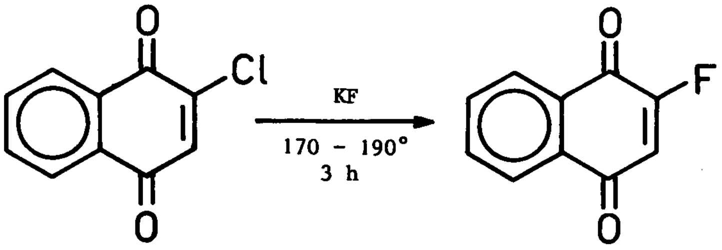
anhydrous ether (25.0 ml). The mixture was allowed to stir a further 10 min. while the temperature was maintained at 0-5°. During this time, the insoluble 1-acyl-2-phenylhydrazine precipitated as a white solid. While the solution was still cold, the product was filtered and washed with sparing amounts of cold ether. If desired, the material could be recrystallized from aqueous alcohol.

Acknowledgements.- This work was supported by grants from Wellesley College and by the donors of the Susan E. Gray Memorial Fund. We thank the Merck Foundation for generous assistance.

2-FLUORO-1,4-NAPHTHALENEDIONE

Submitted by R. S. Thomas Loeffler* and Carolyn S. James
(3/14/80)
University of Bristol
Long Ashton Research Station
Bristol, BS18 9AF, ENGLAND

As a result of interest in structure-activity relationships of quinone fungicides,[1] we wished to prepare a series of 2-fluoro-3-alkyl-1,4-naphthalenedione. Although the parent compound, 2-fluoro-1,4-naphthalenedione, had been used in a study of the effects of substances on dental decay,[2] no details of its preparation or references were given. The only other report of the compound was of its detection as an intermediate in the polarogrphic reduction of 2,3-difluoro-1,4-naphthalenedione.[3] We found that 2-fluoro-1,4-naphthalenedione could be obtained in good yield by a



halogen-exchange reaction between potassium fluoride and 2-chloro-1,4-naphthalenedione.

EXPERIMENTAL

2-Fluoro-1,4-naphthalenedione.- Potassium fluoride (commercial "anhydrous") was dried at 100° under reduced pressure (< 3 torr.) for 4 hr, and 2-chloro-1,4-naphthalenedione[4] was dried in a desiccator over potassium hydroxide pellets for 24 hrs. The chloro quinone (2 g) and dry potassium fluoride (8 g) were ground together using a pestle and mortar, and quickly transferred to a small ampoule, which was sealed and totally immersed in an oil bath previously heated to 180°. The temperature was kept at 170-190° for 3 hrs and the ampoule was cooled, opened, and the brown mixture ground using a pestle and mortar to facilitate extraction with diethyl ether (2 x 50 ml). The extract was filtered to remove potassium salts, washed with water and dried with anhydrous sodium sulphate. After solvent removal the residue was purified by column chromatography on silica gel 60 (Merck); the fluoro quinone was eluted by a mixture of petroleum ether (bp 40-60°) (98 parts by volume) and diethyl ether (2 parts by volume). The fractions containing the product were combined and evaporated to dryness to give 0.74 g (40%) of yellow crystals, mp. 101-102°. ^{1}H nmr ($CDCl_3$): δ7.95-8.25 (m, 2H), 7.7-7.9 (m, 2H), 6.62 (d, 1H, J_{HF} = 12 Hz). ms (70 eV): M^+ 176.

Anal. Calcd. for $C_{10}H_5FO_2$: C, 68.18; H, 2.84.

Found: C, 68.39; H, 2.62.

It is essential that the potassium fluoride used be completely dry; even small amounts of moisture drastically reduce the yield. The ampoule should be as full as possible, and completely immersed in the oil bath, to prevent the 2-chloro-1,4-naphthalenedione subliming out of the reaction mixture. Unless these precautions are taken, mixtures of the chloro- and fluoro quinone result, which are not readily separable by chromatography.

The procedure described above gives 2-fluoro-1,4-naphthalenedione completely free from the 2-chloro compound, as evidenced by the ^{1}H 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