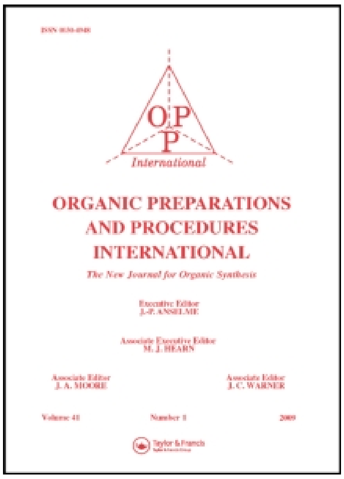

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A CONVENIENT METHOD FOR THE PREPARATION OF 1-ACYL-2-PHENYLHYDRAZINES

Michael J. Hearn[a]; Julia E. Grimwade[a]
[a] Department of Chemistry, Wellesley College, Wellesley, Massachusetts

To cite this Article Hearn, Michael J. and Grimwade, Julia E.(1980) 'A CONVENIENT METHOD FOR THE PREPARATION OF 1-ACYL-2-PHENYLHYDRAZINES', Organic Preparations and Procedures International, 12: 3, 249 — 251

To link to this Article: DOI: 10.1080/00304948009458563

URL: http://dx.doi.org/10.1080/00304948009458563

8. R. J. Gillespie and J. A. Leisten, J. Chem. Soc., 10, (1954).
9. The protection method also may yield yellow crystals, (see ref. 1), which probably indicates the presence of some aniline in the final product.
10. All proton chemical shifts are reported relative to Tiers' salt. (Sodium-2,2-dimethyl-2-silapentane-5-sulfonate.)
11. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, p. 81.
12. The ^{13}C chemical shifts were measured in D_2O relative to p-dioxane and calculated relative to TMS by adding a constant of 66.99 ppm.
13. L. F. Johnson and W. C. Jankowski, "Catalog of C-13 NMR for Organic Chemists," #231, Wiley, New York, N. Y., 1972.

A CONVENIENT METHOD FOR THE PREPARATION OF 1-ACYL-2-PHENYLHYDRAZINES

Submitted by Michael J. Hearn* and Julia E. Grimwade
(12/7/79)
Department of Chemistry
Wellesley College
Wellesley, Massachusetts 02181

Substantial control over the extent of acylation of N,N-dimethylhydrazine with acid chlorides has been achieved by appropriate choice of solvent [E. A. Sedor, R. E. Fries and H. J. Richards, Org. Prep. Proced., 2, 275 (1970)]. The highly exothermic reaction of phenylhydrazine with acid chlorides in dry ether leads to formation of the insoluble 1-acyl-2-phenylhydrazine [R. F. Moore and S. G. P. Plant, J. Chem. Soc. (C), 3475 (1951)]. Although the mesomeric effect of the phenyl group in phenylhydrazine serves to reduce diacylation as a secondary reaction, milder reactions have been sought which would more definitively control the vigorous nature of the acylation. The dropwise addition of an ethereal solution of a carboxylic acid anhydride to a stirred solution of phenylhydrazine in a sparing amount of ether at 0-5° led to the immediate precipitation of the corresponding 1-acyl-2-phenylhydrazine as a white crystalline solid. When the reaction mixture was allowed to stir further and subsequently filtered, the compound was obtained in high yield in spectroscopically pure form (Table).

TABLE. 1-Acyl-2-Phenylhydrazines[†]

Anhydride	Product	mp. (°C)	Yield
$(CH_3CO)_2O$	$CH_3CONHNHPh$	129° (lit 129°)	90%
$(CH_3CH_2CO)_2O$	$CH_3CH_2CONHNHPh$	157° (lit 157°)	91
$(CH_3CH_2CH_2CO)_2O$	$CH_3CH_2CH_2CONHNHPh$	95-96° (lit 103°)	73
$((CH_3)_2CHCO)_2O$	$(CH_3)_2CHCONHNHPh$	139-40° (lit 140°)	86
$(PhCO)_2O$	$PhCONHNHPh$	165-67° (lit 168°)	86

[†] Literature values from F. Wild, "Characterization of Organic Compounds," pp. 151-2, 172, Cambridge University Press, 1947.

The materials were suitable for further transformations without prior purification. Maximum yields and purities were observed when the cold reaction mixture was worked up at once. Prolonged reaction times at room temperature led to the formation of dark liquids, presumably the result of overacylation, from which we were not able to isolate the 1-acyl-2-phenylhydrazines.

EXPERIMENTAL

General Procedure.- To a rapidly stirred solution of phenylhydrazine (18 mmoles) in anhydrous ether (2.5 ml) cooled in an ice-water mixture was added over a period of 10 min. the carboxylic acid anhydride (40 mmoles) in 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