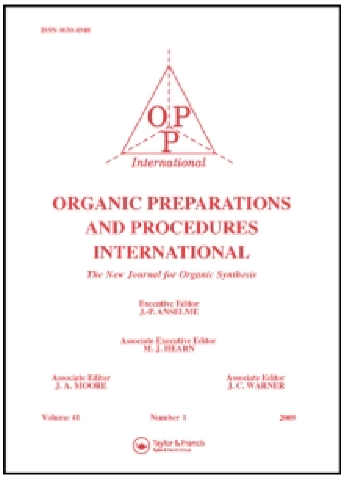

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A FACILE SYNTHESIS OF DIARYLACETONITRILE FROM DIARYKETONES AND TRIMETHYLSILYL CYANIDE

Katsuhiro Saito[a]; Shinzo Kagabu[b]; Yoichi Horie[a]; Kensuke Takahashi[a]
[a] Department of Applied Chemistry, Nagoya Institute of Technology, Nagoya, JAPAN [b] Department of Chemistry, Faculty of Education, Gifu University, Gifu, JAPAN

To cite this Article Saito, Katsuhiro , Kagabu, Shinzo , Horie, Yoichi and Takahashi, Kensuke(1989) 'A FACILE SYNTHESIS OF DIARYLACETONITRILE FROM DIARYKETONES AND TRIMETHYLSILYL CYANIDE', Organic Preparations and Procedures International, 21: 3, 354 — 355

To link to this Article: DOI: 10.1080/00304948909356395

URL: http://dx.doi.org/10.1080/00304948909356395

A FACILE SYNTHESIS OF DIARYLACETONITRILE FROM DIARYKETONES AND TRIMETHYLSILYL CYANIDE

Submitted by (07/13/88)

Katsuhiro Saito,* Shinzo Kagabu†,
Yoichi Horie and Kensuke Takahashi

Department of Applied Chemistry,
Nagoya Institute of Technology,
Showa-ku, Nagoya 466, JAPAN

† Department of Chemistry, Faculty of Education,
Gifu University, Yanagido, Gifu 501-11, JAPAN

Introduction of the nitrile group into organic compounds is a very valuable technique in organic synthesis. Conversion of carbonyl compounds into nitrile compounds has been investigated actively and a wide variety of methods have been developed. Trimethylsilyl cyanide proved to be very effective to transform carbonyl compounds into α-cyanohydrins.[1] However, reduction of the hydroxy group of the cyanohydrins requires conversion of the cyanohydrins to α-halonitriles, which are then reduced with zinc.[2]

We now report that diarylketones (1) may be converted into diarylacetonitriles (3) in moderate yields,[3] via the reaction of trimethylsilyl cyanide with the sodium salts of diarylketone tosylhydrazones (2), very easily prepared in quantitative yields from 1 and tosylhydrazide.[4] The procedure is a simple one-pot reaction which requires only addition of sodium hydride and trimethylsilyl cyanide to a diglyme solution of the tosylhydrazone.

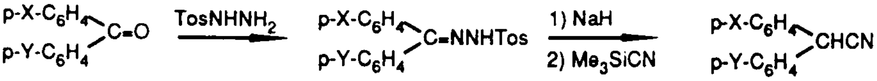

TABLE. Yields of Diarylacetonitriles (3)[5]

2	X	Y	Yields of 3[a] (%)	IR (CN) (cm^{-1})
2a	H	H	49	2222
2b	H	Cl	43	2221
2c	H	OMe	52	2220
2d	OMe	OMe	51	2223

a) All the yields are isolated yields based on 2.

EXPERIMENTAL SECTION

Reaction of Sodium Salt of Benzophenonetosylhydrazone (2a) with Trimethylsilyl Cyanide. Representative Procedure.- To a solution of 2a (7.36 g, 20 mmol) in anhydrous diglyme (50 ml) was added sodium hydride (50% in oil, 0.72 g, 30 mmol). After evolution of hydrogen gas had ceased, trimethylsilyl cyanide (9.90 g, 100 mmol) was added and the mixture was heated at 125° for 5 min. to evolve a quantitative amount of nitrogen gas. After filtration the filtrate was diluted with ether (200 ml), washed with water (200 ml x 5), dried over anhydrous sodium sulfate, and finally the solvent was evaporated on a rotary evaporator. The oily residue was chromatographed on silica gel (hexane-benzene 6:4) to give 3a (1.87 g, 49%).

Acknowledgement.- The authors are indebted to Professor Paul G. Gassman of the University of Minnesota for fruitful suggestions.

REFERENCES

1. D. A. Evans, J. M. Hoffman and L. K. Truesdale, J. Am. Chem. Soc., 95, 5822 (1973); J. K. Rasmussen and S. M. Heilmann, Synthesis, 219 (1978); P. G. Gassman and J. J. Talley, Tetrahedron Lett., 3773 (1978); P. G. Gassman, K Saito and J. J. Talley, J. Am. Chem, Soc., 102, 7613 (1980); P. G. Gassman and K. Saito, Tetrahedron Lett., 22, 1311 (1981); K. Saito and H. Kojima, Bull. Chem. Soc. Jpn., 58, 1918 (1985).

2. A. J. Hignett and F. W. Kay, Chem. Ind. (London), 54, 98T (1935).

3. Benzaldehyde, acetophenone, propiophenone and dibenzylketone did not afford the corresponding nitriles by this method.

4. W. R. Bamford and T. S. Stevens, J. Chem. Soc., 4735 (1952); D. G. Farnum, J. Org. Chem., 28, 870 (1963); K. Saito, T. Toda and T. Mukai, Bull. Chem. Soc. Jpn., 57, 1567 (1984).

5. The nitriles (3) were reported in the literature [K. Sisido, H. Nozaki, M. Nozaki and K. Okano, J. Org. Chem., 19, 1699 (1954) and G. Sumrell and G. E. Goheen, J. Am. Chem. Soc., 77, 3805 (1955)].

****

AN IMPROVED PROCEDURE FOR THE DICHLOROACETYLATION OF PRIMARY AND SECONDARY AMINES[†]

Submitted by (04/18/88)
Braja G. Hazra*, V. S. Pore and S. P. Maybhate

National Chemical Laboratory
Pune 411 008, INDIA

The dichloroacetamido moiety ($-NHCOCHCl_2$) is prevalent in number of biologically