This article was downloaded by: [The Aga Khan University] On: 21 October 2014, At: 00:44 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

THE REACTION OF α,α,α-TRIFLUOROMETHOXYBENZENE WITH AICI₃: A HIGH YIELD PREPARATION OF α,α,α-TRICHLOROMETHOXYBENZENE

Qiliang Chen^a, Jie Xu^a & Wei Zhang^a ^a Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China Published online: 16 Aug 2006.

To cite this article: Qiliang Chen , Jie Xu & Wei Zhang (2002) THE REACTION OF a,a,a-TRIFLUOROMETHOXYBENZENE WITH AICI₃: A HIGH YIELD PREPARATION OF a,a,a-TRICHLOROMETHOXYBENZENE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:5, 799-801, DOI: <u>10.1081/</u><u>SCC-120002522</u>

To link to this article: <u>http://dx.doi.org/10.1081/SCC-120002522</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

SYNTHETIC COMMUNICATIONS, 32(5), 799-801 (2002)

THE REACTION OF α,α,α-TRIFLUOROMETHOXYBENZENE WITH AICl₃: A HIGH YIELD PREPARATION OF α,α,α-TRICHLOROMETHOXYBENZENE

Qiliang Chen,* Jie Xu, and Wei Zhang

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

ABSTRACT

 α, α, α -Trifluoromethoxybenzene was allowed to react with AlCl₃ in CH₂Cl₂ to afford α, α, α -trichloromethoxybenzene in excellent yield and purity.

Numerous chemical transformations have demonstrated the unusual stability of the OCF₃ group to strong acids and bases, as well as to strong oxidizing and reducing conditions.^{1–2} As far as substitution, the OCF₃ group is similar to the halogens such as bromine and chlorine, and clearly indicates a deactivating effect on the aromatic ring. It was found that the OCF₃ group orients attacking electrophilic reagents to the ortho/para position. For example, the nitration of α, α, α -trifluoromethoxybenzene (TFMB) under usual condition with a mixture of nitric and sulfuric acids gave para/ortho substitution. However, when α, α, α -trifluoromethoxybenzene reacted with acetyl chloride using aluminum chloride as a catalyst,

799

Copyright © 2002 by Marcel Dekker, Inc.

www.dekker.com

^{*}Corresponding author. E-mail: chenql@mail.dlptt.ln.cn

ORDER		REPRINTS
-------	--	----------

CHEN, XU, AND ZHANG

besides the expected 4-acetyl- α , α , α -trifluoromethoxybenzene (PATFMB), the reaction also produced α, α, α -chlorodifluoromethoxybenzene and α, α, α dichlorofluoromethoxybenzene respectively.³ In the present work, the α, α, α -trichloromethoxybenzene (TCMB), which has received extensive interest in pharmaceutical and agrochemical industry (as pesticides), was prepared by the reaction of α, α, α -trifluoromethoxybenzene with aluminum chloride (Scheme 1), the results in this communication were summarized in Table 1.



The data suggested that in the aluminum chloride catalyzed acetylation of α, α, α -trifluoromethoxybenzene, which took place in CH₂Cl₂, CH₂CH₂Cl₂ and CCl₄ solvent, respectively, the amount of 4-acetyl- α, α, α -trifluoromethoxybenzene afforded was low. Instead, α, α, α -trichloromethoxybenzene was obtained as the major product. In the control experiment, the reaction of α, α, α -trifluoromethoxybenzene with aluminum chloride in CH_2Cl_2 yielded α, α, α -trichloromethoxybenzene in excellent yield and purity, producing only $1.8\% \alpha, \alpha, \alpha$ -dichlorofluoromethoxybenzene

				Time	Product (%)		
Entry	Reagent	Catalyst	Solvent	(h)	PATFMB	ТСМВ	DCFMB
1	CH ₃ COCl	AlCl ₃	CH ₂ Cl ₂	2	25	75	_
2	CH ₃ COCl	AlCl ₃	$CH_2CH_2Cl_2$	2	22.5	77.5	_
3	CH ₃ COCl	AlCl ₃	CCl ₄	2	20	80	_
4	_	AlCl ₃	CH_2Cl_2	0.5	-	98.2	1.8

Table 1. AlCl₃ Catalyzed Acetylation of α, α, α -Trifluoromethoxybenzene with Acetyl Chloride





ORDER		REPRINTS
-------	--	----------

PREPARATION OF TCMB

(DCFMB) and no α, α, α -chlorodifluoromethoxybenzene. From these results, it was, therefore, concluded that the primary reaction is an exchange of halogen atoms between α, α, α -trifluoromethoxybenzene and aluminum chloride. This reaction provides a simple and efficient method for the preparation of α, α, α -trichloromethoxybenzene.

EXPERIMENTAL

Preparation of TCMB. To a cooled (0°C) and stirred solution of anhyd. AlCl₃ (0.15 mol) in CH₂Cl₂ (15 ml), α,α,α -trifluoromethoxybenzene (0.049 mol) was added and it was stirred at 0–10°C for 0.5 h, then poured it into the mixture of ice with HCl, stirred for 5 min, separated the lower layer, the aqueous solution was extracted with dichloromethane (10 ml × 2), combined organic phase was washed with water, dried over MgSO₄ and filtered. After removed the solvent, distillation of the solution in vacuo (15 mmHg, 100–103°C) gave the pure α,α,α -trichloromethoxybenzene (yield: 85%, purity: 98%). Anal. for C₇H₅Cl₃O: Calc. C 39.81%, H 2.37%, found: C 39.51%, H 2.30%, MS *m*/*z* (assignment, %) 216 (C₇H₅³⁷Cl₃O, 6), 212 (C₇H₅³⁵Cl₂³⁷ClO, 21.2), 210 (C₇H₅³⁵Cl₃O, 22.7), 179 (C₇H₅³⁷Cl₂O, 7.5), 177 (C₇H₅³⁵Cl³⁷ClO, 50), 175 (C₇H₅³⁵Cl₂O, 83), 141 (C₇H₄³⁷ClO, 4.5), 139 (C₇H₄³⁵ClO, 15), 117 (C³⁵Cl₃, 53), 77 (C₆H₅, 100). ¹H NMR (CCl₄): (δ ppm) 8.1–8.2 (1H, *p*, ArH), 7.4–7.6 (2H, *o*, ArH), 7.2–7.4 (2H, *m*, ArH).

REFERENCES

- 1. Sheppard, W.A. J. Org. Chem. 1964, 29(1), 3-11.
- 2. Yagupolsky, L.M. Dokl. Akad. Nauk. SSSR. 1955, 105(1), 100-102.
- George, A. Olah; Takehilco Yamato, et al. J. Am. Chem. Soc. 1987, 109, 3708–3713.

Received in Japan December 20, 2000



801

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the <u>U.S. Copyright Office</u> for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on <u>Fair Use in the Classroom</u>.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our <u>Website</u> <u>User Agreement</u> for more details.

Order now!

Reprints of this article can also be ordered at http://www.dekker.com/servlet/product/DOI/101081SCC120002522