

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

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



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

S-ALKYLATION OF THIOACRIDONE DERIVATIVES USING SOLID-LIQUID PHASE TRANSFER CATALYSIS WITHOUT SOLVENT

Mircea Vlassa^a; Maria Kezdi^a

^a Institute of Chemistry Cluj-Napoca, Cluj-Napoca, ROMANIA

To cite this Article Vlassa, Mircea and Kezdi, Maria(1987) 'S-ALKYLATION OF THIOACRIDONE DERIVATIVES USING SOLID-LIQUID PHASE TRANSFER CATALYSIS WITHOUT SOLVENT', *Organic Preparations and Procedures International*, 19: 6, 433 – 435

To link to this Article: DOI: 10.1080/00304948709356204

URL: <http://dx.doi.org/10.1080/00304948709356204>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

OPPI BRIEFS

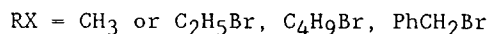
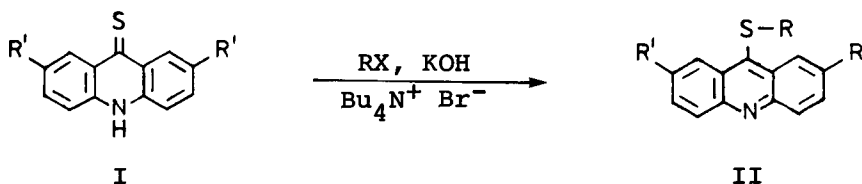
S-ALKYLATION OF THIOACRIDONE DERIVATIVES USING SOLID-LIQUID PHASE TRANSFER CATALYSIS WITHOUT SOLVENT[†]

Submitted by Mircea Vlassa* and Maria Kezdi
(02/03/86)

Institute of Chemistry Cluj-Napoca
str. Fintinele 30
3400 Cluj-Napoca, ROMANIA

S-Alkylthioacridines have been obtained by heating thioacridone with alkyl bromides or iodides in presence of sodium alkoxide or in aqueous-alcoholic sodium hydroxide^{1,2} and by liquid-liquid phase-transfer catalysis.³ It has been shown that acetate,⁴ alkoxide,⁵ fluoride,⁶ indole,⁷ and pyrimidine and purine derivatives⁸ can be efficiently alkylated without solvent in the presence of quaternary ammonium salts.

As a continuation of our phase-transfer studies, we prepared several S-alkyl thioacridines (Table). As in the case of liquid-liquid phase-



transfer catalysis, only S-alkylation occurred as demonstrated by UV and the absence of C=S vibrations in their IR spectra. The present procedure offers the advantage of yields higher or comparable to those of other methods and of easier work-ups and requires no heat (except for IIc, see Table) or solvent.

EXPERIMENTAL SECTION

Melting points are not corrected. The IR spectra were recorded as KBr pellets on a Unicam SP 200 spectrophotometer and the UV spectra were

determined in MeOH on a Carl Zeiss Specord spectrometer. TLC analyses were run on plates coated with silica gel and eluted with C₆H₆-EtOH (10:1); the visualising agent was iodine.

General Procedure.- The thioacridone derivative (1 mmol), finely ground KOH (122 mg, 2 mmol) and tetrabutylammonium bromide (32 mg, 0.1 mmol) were mixed well. The alkylating agent (2 mmol) was added and resulting mixture was shaken at 25° for 1 hr. then left standing for the appropriate time (see Table). In the case of IIa-IId, the mixture was diluted with ether, then filtered through a short column of silica gel (3.5 g). The ethereal solution was evaporated and the residue was purified by recrystallization from aq. EtOH (for IIa and IIc), light petroleum (for IIb) or EtOH (for IIId). For IIe-IIg, the mixture was diluted with water, the precipitate was collected, washed well with water, dried and the residue recrystallized from CHCl₃-EtOH.

TABLE. S-Alkylated Thioacridines (IIa-g)

Cmpd	R	R'	Yield (%)	Temp. (°C)	Time (hrs.)	mp. (°C)	lit. mp. (°C)
IIa	CH ₃	H	85	25	72 ^a	112-114	113-114 ^b
IIb	C ₂ H ₅	H	75	25	72	64-66	63 ^c
IIc	C ₄ H ₉	H	80	75	24	79-80	74 ^d
IIId	PhCH ₂	H	90	25	48	107-109	109 ^b
IIe	CH ₃	Br	90	25	72	216-217	215 ^e
IIIf	C ₂ H ₅	Br	70	25	72	174-176	174 ^e
IIg	PhCH ₂	Br	90	25	72	202-203	199-200 ^e

a) No yield without catalyst. b) Ref. 1. c) Ref. 2a. d) Ref. 3a. e) Ref. 2b.

REFERENCES

- + Part V, M. Vlassa and M. Kezdi, J. prakt. Chem., In press.
1. A. Edinger and W. Arnold, *ibid.*, 64, 182 (1901).
 2. a) A. Edinger and J. C. Ritsema, *ibid.*, 68, 72 (1903); b) M. Ionescu, I. Goia and H. Mantsch, *Studii si Cercetari de Chimie (Cluj, Romania)*, 13, 95 (1965); *Chem. Abstr.*, 60, 5456 (1964).
 3. a) J.-P. Galy, E.-J. Vincent, A.-M. Galy, J. Barbe and J. Elguero,

- Bull. Soc. Chim. Belges, 90, 947 (1981); b) M. Vlassa, M. Kezdi and I. Goia, *Synthesis*, 850 (1980).
4. J. Barry, G. Bram, G. Decodts, A. Loupy, P. Pigeon and J. Sansoulet, *Tetrahedron*, 39, 2673 (1983).
 5. J. Barry, G. Bram, G. Decodts, A. Loupy, P. Pigeon and J. Sansoulet, *ibid.*, 40, 2945 (1984).
 6. P. Pigeon, Dissertation, Université Paris-Sud, 1984.
 7. J. Barry, G. Bram, G. Decodts, A. Loupy, P. Pigeon and J. Sansoulet, *Tetrahedron*, 39, 2669 (1983).
 8. G. Bram, G. Decodts, Y. Bensaid, C. Combet Farnoux, H. Galons and M. Miocque, *Synthesis*, 543 (1985).

SYNTHESIS OF γ,δ -UNSATURATED KETONES

Submitted by Thomas C. McKenzie
(10/27/86)
Department of Chemistry
University of Alabama
Tuscaloosa, AL 35487

In connection with ongoing synthetic studies, we required a variety of γ,δ -unsaturated methyl ketones. Compounds of this type have been prepared by the Claisen rearrangement of allyl vinyl ethers,¹ via alkylation of ketimines with allylic halides,² and by the conjugate addition of vinyl cuprates to enones.³ We now report a convenient, one-step synthesis of γ,δ -unsaturated ketones from allylic alcohols via the Claisen rearrangement.