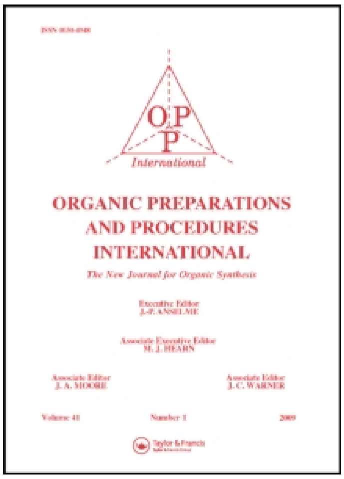

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S-ALKYLATION OF THIOACRIDONE DERIVATIVES USING SOLID-LIQUID PHASE TRANSFER CATALYSIS WITHOUT SOLVENT

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OPPI BRIEFS

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

Submitted by (02/03/86)
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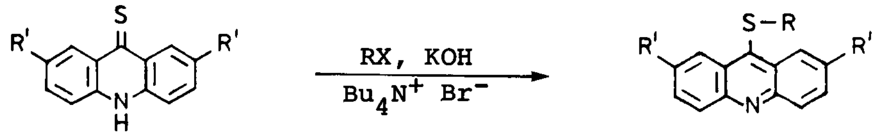
S-Alkylthioacridines have been obtained by heating thioacridone with alkyl bromides or iodides in presence of sodium alkoxide or in aqueous-alcoholic sodium hydroxide[1,2] and by liquid-liquid phase-transfer catalysis.[3] It has been shown that acetate,[4] alkoxide,[5] fluoride,[6] indole,[7] and pyrimidine and purine derivatives[8] 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.



I II

RX = CH_3 or C_2H_5Br, C_4H_9Br, $PhCH_2Br$

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 C_6H_6-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 IId). For IIe-IIg, the mixture was diluted with water, the precipitate was collected, washed well with water, dried and the residue recrystallized from $CHCl_3$-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_2H_5	H	75	25	72	64-66	63[c]
IIc	C_4H_9	H	80	75	24	79-80	74[d]
IId	$PhCH_2$	H	90	25	48	107-109	109[b]
IIe	CH_3	Br	90	25	72	216-217	215[e]
IIf	C_2H_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.

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SYNTHESIS OF γ,δ-UNSATURATED KETONES

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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.