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PYROLYSIS OF β-HYDROXY-α-BROMOSULFOXIDES: A SIMPLE SYNTHESIS OF BROMOMETHYL KETONES

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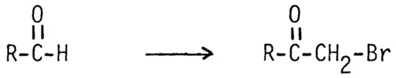
The reaction of lithio bromomethyl phenyl sulfoxide with aldehydes gave the corresponding β-hydroxy-α-bromosulfoxides. Pyrolysis of these hydroxysulfoxides yielded the expected bromemethyl ketones in excellent yields.

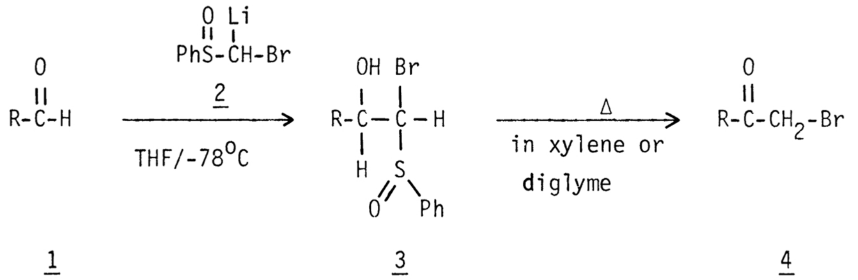
Syntheses of halomethyl ketones have been a subject of current interest due to their wide applications in organic syntheses. Methods[1] for the syntheses of α-halocarbonyl compounds have been reported. However, there are very few methods[2] for specific syntheses of halomethyl ketones. Our interest in the chemistry of α-halosulfoxides led to the development of bromomethyl phenyl sulfoxide as an agent for specific synthesis of bromomethyl ketones from the corresponding aldehydes (equation 1).



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}H \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}Br} \qquad (1)$$

R = alkyl or aryl

Our novel approach involves the reaction of aldehyde 1 with lithio bromomethyl phenyl sulfoxide 2 in tetrahydrofuran (THF) at -78°C, followed by the pyrolytic elimination of the β-hydroxy-α-bromosulfoxide 3 to give bromomethyl ketones 4 in excellent yield (equation 2).

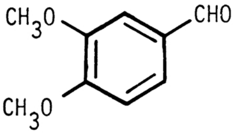
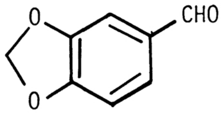
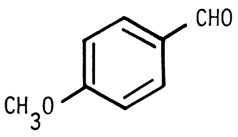


(2)

Bromomethyl phenyl sulfoxide was prepared according to the procedure of Iriuchijima and Tsuchihashi.[3] The lithio compound 2 was successfully generated with lithium diisopropylamide (LDA) in THF at -78°C. Butyllithium led to extensive decomposition of the α-bromosulfoxide.[4] Addition of octanal (1.0 equiv.) to the THF solution of 2 at -78°C gave a pale yellow homogeneous mixture which was maintained at this temperature for 4 hr before being quenched with water. The aqueous solution was extracted with chloroform and the crude product was recrystallized from chloroform-hexane (4:1) to give 1-bromo-1-phenylsulfinyl-2--nonanol (74% yield). Pyrolysis,[5] under nitrogen, of the hydroxysulfoxide in xylene (160°C) gave bromomethyl heptyl ketone in 99% yield (isolated by preparative thin layer chromatography, PLC, on Merck PF_{254} silica gel; 1:9 chloroformhexane). In the cases of aryl hydroxysulfoxides 3 (R = aryl), pyrolysis in diglyme gave higher yields of the corresponding bromomethyl ketones. The results are summarized in Table 1.

Further study on the applications of bromomethyl phenyl sulfoxide in organic synthesis is in progress.

Table 1

Aldehydes	3, Yields % (Mp. °C)	4, Yield[c] % (Method)[d] NMR
$C_5H_{11}CHO$	71 (106)[a]	91(1)[0.8-1.9 (9H, m), 2.6(2H, t, J=7Hz), 3.9(2H,s)]
$C_7H_{15}CHO$	74 (119)[a]	99(1)[0.6-1.9 (13H, m), 2.6(2H, t, J=7Hz), 3.9(2H,s)]
$C_{13}H_{27}CHO$	67 (102)[a]	97(1)[0.6-1.9 (25H, m), 2.4(2H, t, J=10Hz), 3.9(2H,s)]
	85 (118, dec.)[b]	86(2)[4.0(6H,s), 4.4(2H,s), 6.9(1H, d, J=9Hz), 7.6(2H,m)]
	79 (191, dec.)[b]	88(2)[4.4(2H,s), 6.1(2H,s), 6.9(1H, d, J=9Hz), 7.5(2H,m)]
	85 (122, dec.)[b]	88(2)[3.9(3H,s), 4.5(2H,s), 7.2(2H, d, J=5Hz), 8.2 (2H, d, J=5Hz)]

[a] Products were purified on recrystallization from 4:1 chloroform-hexane.

[b] Products were recrystallized from 4:1 chloroform-ether.

[c] Products were isolated by PLC; 1:9 chloroform-hexane.

[d] Method 1, heat in xylene; 2, heat in diglyme.

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