INTRAMOLECULAR ACYLATION OF α-SULFINYL CARBANION: SYNTHESES OF CYCLOHEXENONES AND α-METHYLENE CYCLOPENTENONES

BY

SIRIRAT CHANCHARUNEE

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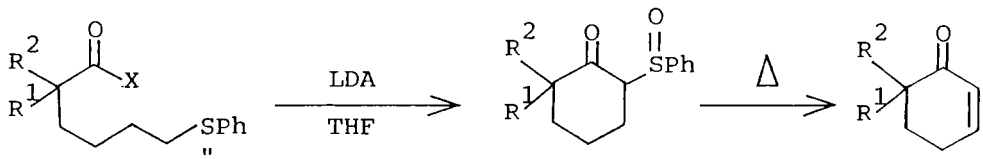
ABSTRACT

α-Sulfinyl carbanions derived from the sulfoxides 17 and 18 underwent intramolecular acylation to give the β-ketosulfoxides 19 and 20 which upon pyrolysis afforded the 6,6-disubstituted cyclohexenones 15 and 6-monosubstituted cyclohexenones 16 respectively in high yield.

The present method was used to prepare ketosulfoxides 47 (derived from intramolecular acylation of sulfoxides 46) which upon pyrolysis gave highly substituted cyclopentenones 45 in high yield.

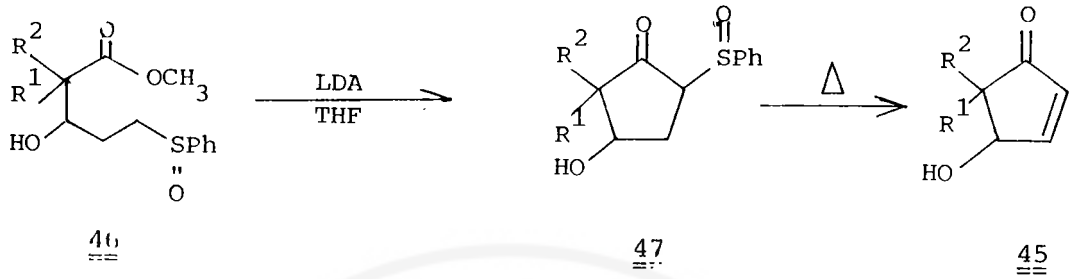
The intramolecular acylation of α-sulfinyl carbanions derived from sulfoxides 33 gave 34 which readily dehydrated to give the functionalized cyclopentenones 35 in high yields. Alkylation and subsequent pyrolysis of 35 afforded α-alkylidene cyclopentenones 49 including Methylenomycin B in moderate to good yields. Moreover, Michael addition of 35 ($R^1 = CH_3$, $R^2 = H$) with nitronate anion derived from nitromethane afforded ketosulfoxide 55 which upon pyrolysis gave the cyclopentenone 56.



17, X = O, R^1; $R^2 \neq H$ 19, R^1; $R^2 \neq H$ 15, R^1; $R^2 \neq H$

18, X = NCH_3, R^1 = alkyl; R^2 = H 20, R^1 = alkyl; R^2 = H 16, R^1 = alkyl; R^2 = H

Ph



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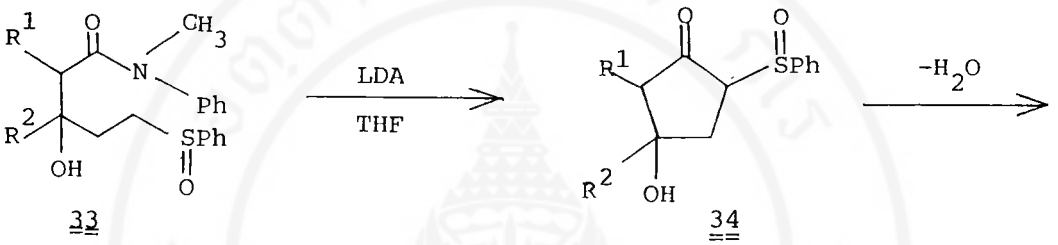

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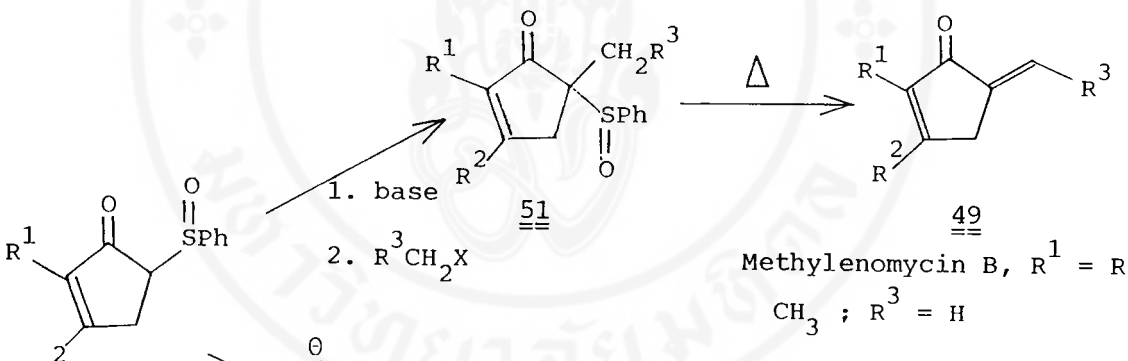
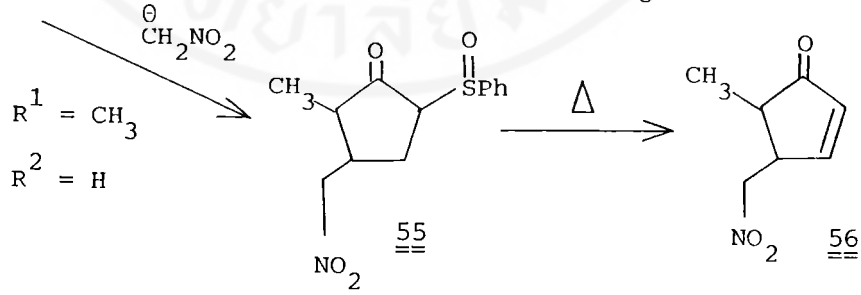


51 49

Methylenomycin B, $R^1 = R^2 = CH_3$; $R^3 = H$

35



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