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CYCLOAROMATIZATION OF α-OXOKETENDITHIOACETALS WITH BENZYLMAGNESIUM CHLORIDE: A NOVEL NAPHTHALENE ANNELATION REACTION

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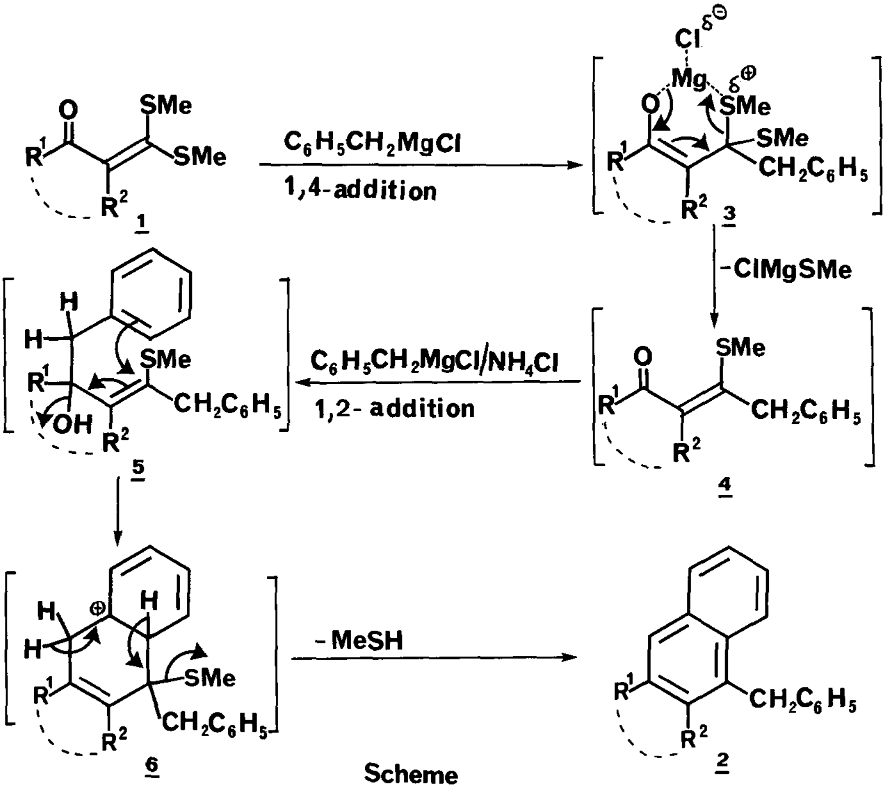
Summary:- α-Oxoketendithioacetals derived from acyclic and cyclic ketones are shown to react with benzylmagnesium chloride to give novel naphthoannelated aromatic compounds by sequential 1,4- and 1,2-additions followed by subsequent cycloaromatization of the resulting carbinols.

In our previous communication, we had reported[1] a versatile approach for benzoannelation of active methylene ketones via α-oxoketendithioacetals, through their reactions with allylmagnesium bromide, followed by Lewis acid catalyzed cyclization. From these results we reasoned that the reaction of benzylmagnesium halide with α-oxoketendithioacetals should yield, through aromatic ring participation, a wide variety of naphthoannelated products depending on the structural characteristics of α-oxoketendithioacetals. We now report the results of our preliminary studies in this communication.

When 1a was reacted with benzylmagnesium chloride (1.25 eqv),the reaction mixture after work-up and subsequent treatment with borontrifluoride etherate afforded a viscous liquid, which was purified by column chromatography to give a white solid, m.p. 106°, along with the unreacted starting material 1a (35%). The product was characterized as 9-benzyl-1,2,3,4-tetrahydroanthracene 2a(31%) on the basis of spectral and analytical data,M$^+$(mass)m/z: 272 ($C_{21}H_{20}$); i.r.(KBr) 1610(m), 1500(s) cm^{-1}; ^{1}H-n.m.r. (CCl_4) δ 1.45-1.90 (m, 4H); 2.50-3.00 (m, 4H); 4.32 (s, 2H, benzylic CH_2); 6.60-7.85 (m, 10H, aromatic). From the structure of 2a, it was apparent that two equivalents of benzylmagnesium chloride have been used for each mole of 1a. Thus, in another experiment, when 1a was reacted with three equivalents of benzylmagnesium chloride, the yield of 2a was increased to 81% with no trace of unreacted starting material. Similarly, the other cyclic ketendithioacetals 1b-f were reacted with three eqv. of benzylmagnesium chloride to afford the corresponding benzylsubstituted naphthoannelated products 2b-f in good yields (Table).[2] The α-oxoketendithioacetals 1g-i derived from open-chain active methylene ketones similarly yielded the corresponding substituted naphthalene derivatives 2g-i in 59-65% overall yields.[2] Under similar reaction conditions, 1j derived from 2-acetylnaphthalene yielded the corresponding binaphthyl derivative 2j.[2]

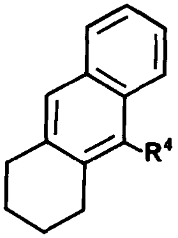
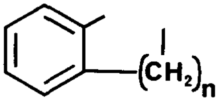
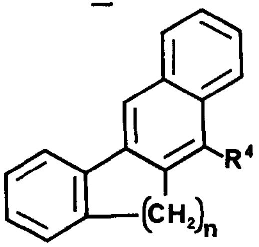
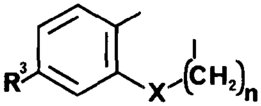
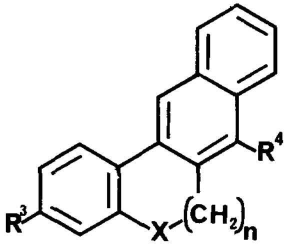
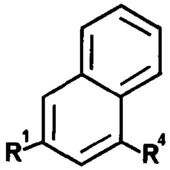
The probable mechanism for the formation of 2 from 1 is shown in the scheme. Apparently, the benzylmagnesium chloride undergoes initial 1,4-conjugate addition to give β-benzyl-β-methylthioalkenylketones 4, which compete with 1 to react with benzylmagnesium chloride via preferential 1,2-addition yielding the corresponding carbinols 5 in the overall reaction sequence.[3,4] Subsequent $BF_3.Et_2O$ catalyzed cyclodehydration of the carbinols 5 affords 2 in good yields.



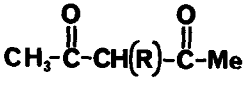
Scheme

The overall transformation could be considered as aromatic annelation of active methylene ketones to naphthalene derivatives via α-oxoketendithioacetals. It is pertinent to note that recently, a few synthetic approaches for benzene derivatives involving combination of 1,3-electrophilic and 1,3-nucleophilic fragments have been developed.[1] However, similar synthetic routes for naphthalene derivatives have been few in number. Thus a few of the polymethyl naphthalene derivatives have been obtained by the reaction of substituted benzylmagnesium chloride with 2,4-pentanediones[5] (7) or β-oxoacetal(8)[6] followed by subsequent cyclodehydration of the resulting β-hydroxyketones or

Table

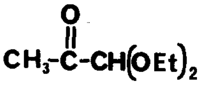
Entry	Starting Material	R^1	R^2	Product	Yield %	m.p. °C
						
1	1a	$-(CH_2)_4-$		2a	81	106
						
2	1b	n=1		2b n=1	62	187
3	1c	n=2		2c n=2	71	108
						
4	1d	$R^3 = H$, X=S; n=1		2d $R^3 = H$, X=S; n=1	58	93–94
5	1e	$R^3 = CH_3$, X=S; n=2		2e $R^3 = CH_3$, X=S; n=2	68	110
6	1f	$R^3 = H$, X=O; n=2		2f $R^3 = H$, X=O; n=2	67	155
						
7	1g	C_6H_5	H	2g $R^1 = C_6H_5$	59	119
8	1h	$pMeOC_6H_4$	H	2h $R^1 = pMeOC_6H_4$	61	115
9	1i	$pMeC_6H_4$	H	2i $R^1 = pMeC_6H_4$	65	112
10	1j	β-naphthyl	H	2j R^1 = β-naphthyl	58	190

$R^4 = -CH_2C_6H_5$



$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH(R)-\overset{\overset{O}{\|}}{C}-Me}$

7, R=H,Me



$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH(OEt)_2}$

8

β-hydroxyacetal respectively. In the present reaction, the α-oxoketendithioacetals which are easily prepared in high yields, in one pot reaction from wide structural variants of active methylene ketones have been shown to be useful 1,3-electrophilic three carbon fragments for the synthesis of novel substituted naphthalene derivatives and polycyclic aromatic compounds. Further work to study the scope of the method and to direct the reaction to exclusive 1,2-addition is in progress.

In a typical experiment, a solution of 1a (1.01g, 0.005 mol) in 25 ml of dry ether was added to a solution of benzylmagnesium chloride (0.015 mol) in 60 ml of ether at 0-5° under N_2 atmosphere. The reaction mixture was further stirred for 45 min and then decomposed with saturated ammonium chloride solution (50 ml), extracted with ether, dried (Na_2SO_4) and evaporated to give the crude carbinol 5a (1.61g, 95%) which was dissolved in dry benzene (40 ml) and borontrifluoride etherate (2 ml) and refluxed for 30 min. The reaction mixture was then poured over cold saturated $NaHCO_3$ solution, extracted with $CHCl_3$ (2x75 ml), washed (H_2O), dried and evaporated to give a viscous residue which was purified by passing through silica gel column (hexane as eluent) to give 2a (1.10g, 81%);m.p. 106°C.

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1. G. Singh, H. Ila and H. Junjappa, Tetrahedron Lett., 25, 5095 (1984).
2. All the compounds were characterized with the help of spectral and analytical data.
3. Our attempts to isolate either the carbinol 5 or the β-methylthioalkenylketones 4 in these reactions were unsuccessful.
4. The alkylthiomethylene ketones are known to undergo ready 1,2-addition with organolithium compounds; P.R. Bernstein, Tetrahedron Lett., 20,1015 (1979).
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