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REACTION OF C_α–C_β-CLEAVAGE IN THE SERIES OF MONOSUBSTITUTED β-DICARBONYL COMPOUNDS

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Summary

Interaction of PhMgBr with α-monosubstituted β-dicarbonyl compounds, β-diketones, β-ketonic esters and β-diesters, is studied. A new reaction route, C_α–C_β-cleavage, the course of which is determined by the pK_{R^+} value of the α-substituent and the pK_a value of the corresponding proton analog of the β-substituent is found.

Introduction of the ferrocenyl substituent into a molecule of an organic compound frequently has a significant effect on the reaction capability of the latter. The recently-discovered reaction route, C_α–C_β-cleavage, in the reaction of some ferrocene-containing β-diketones with Grignard reagents [1] may be accounted for by a specific effect of the ferrocenyl substituent. The readiness of the C_α–C_β-cleavage is related to the ease of α-ferrocenylcarbocation formation [2] in this reaction. Yet, in the case of α-monosubstituted acetoacetic and malonic esters the effect of the ferrocenyl group is insufficient and C_α–C_β-cleavage in the reaction with PhMgBr is not characteristic [3].

In this connection we have studied the interaction of PhMgBr with a number of α-monosubstituted β-dicarbonyl compounds. Some spectral indices of the initial β-dicarbonyl compounds I–XI are given in Table 1.

Formation R^1–Ph (a) is evidence of C_α–C_β-cleavage. The yield of the initial compound with excess PhMgBr indicates the enolization reaction proceeding under these conditions (b). Besides this, addition of a carbonyl group with subsequent formation of a ketonic cleavage product takes place (c).

The experimental data are given in Table 2, the total yield by the three paths mentioned is 80%.

As can be seen from Table 2, the dimethylamino group, a strong stabilizer of the carbocation centre of the +R type in *para*-position on the phenyl ring, leads to fragmentation of compounds I–III irrespective of the β-dicarbonyl part of the substrates. Products of enolization (b) and ketonic cleavage (c) were found in the reaction mixtures (in the case of I).

Benzhydryl derivatives IV–VI do not undergo cleavage under the action of PhMgBr. After decomposition of the reaction mixture by water, only initial com-

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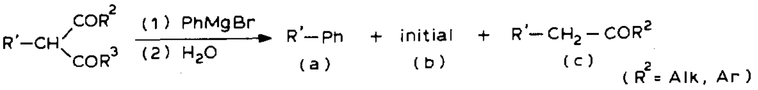
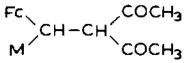
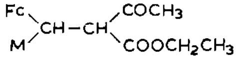
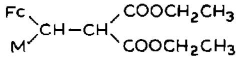
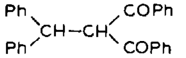
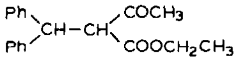
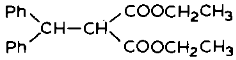
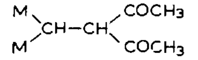
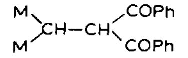
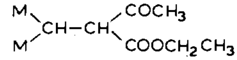
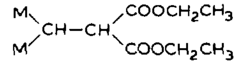
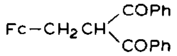
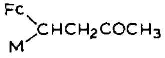
TABLE 1

SPECTRAL DATA FOR COMPOUNDS I–XI.



$$\mathrm{R'{-}CH(COR^2)(COR^3)} \xrightarrow[(2)\ \mathrm{H_2O}]{(1)\ \mathrm{PhMgBr}} \underset{(a)}{\mathrm{R'{-}Ph}} + \underset{(b)}{\text{initial}} + \underset{(c)}{\mathrm{R'{-}CH_2{-}COR^2}} \quad (\mathrm{R^2 = Alk, Ar})$$

No.	Compound ^{a}	^{1}H NMR spectra, δ (ppm)				IR spectra ν(CO)	(cm^{-1})
		H_A	H_B	$COCH_3$	CH_3		
I	 $\mathrm{(Fc)(M)CH{-}CH(COCH_3)_2}$ [4]	4.31	4.31	1.93 2.00		1690	1710
II	 $\mathrm{(Fc)(M)CH{-}CH(COCH_3)(COOCH_2CH_3)}$ [4]	4.30		1.93 2.00	0.97 1.20	1720	1750
III	 $\mathrm{(Fc)(M)CH{-}CH(COOCH_2CH_3)_2}$	4.36 ^{b}			0.98 1.16	1730	1750
IV	 $\mathrm{(Ph)_2CH{-}CH(COPh)_2}$ [5]	5.21	6.40			1710	1670
V	 $\mathrm{(Ph)_2CH{-}CH(COCH_3)(COOCH_2CH_3)}$ [6]	4.77 ^{b}	4.50	2.04	1.00	1730	1765
VI	 $\mathrm{(Ph)_2CH{-}CH(COOCH_2CH_3)_2}$ [7]	4.76 ^{b}	4.36		0.95	1730	1750
VII	 $\mathrm{(M)_2CH{-}CH(COCH_3)_2}$ [8]	4.62	4.62	2.00		1700	1740
VIIa	 $\mathrm{(M)_2CH{-}CH(COPh)_2}$	5.24	6.35			1695	1670
VIII	 $\mathrm{(M)_2CH{-}CH(COCH_3)(COOCH_2CH_3)}$ [8]	4.62	4.40	2.10	1.05	1705	1725
IX	 $\mathrm{(M)_2CH{-}CH(COOCH_2CH_3)_2}$ [8]	4.60 ^{b}	4.20		1.03	1740	1755
X	 $\mathrm{Fc{-}CH_2CH(COPh)_2}$	5.30	3.22				
XI	 $\mathrm{(Fc)(M)CHCH_2COCH_3}$ [4]	4.20	3.05	2.00			

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[a] Fc = $C_{10}H_9Fe$; M = p-$C_6H_4N(CH_3)_2$; ^{1}H NMR spectra in CCl_4, VIIa in CH_2Cl_2; internal standard, TMS. IR spectra in Nujol, II, V, VI, in CCl_4; IV, in CH_2Cl_2. [b] Assigned by deuteration.

TABLE 2

YIELDS OF THE REACTION PRODUCTS OF I–VI WITH PhMgBr

Compound	Yield (%)		
	a	b	c
I	75	traces	traces
II	73	traces	–
III	11	81	–
IV	0	traces	79
V	0	73	–
VI	0	87	–

pounds (b) and products of ketonic cleavage (c) (for IV), were obtained.

While in the cases of I–VI formation of R^1–Ph (a) (or its absence) is the direct indication of C_α–C_β-cleavage (or its absence), in the case of VII–IX the evidence of C_α–C_β-bond fragmentation is shown by the formation of a carbocation M_2CH^+ (λ_{max} 611 nm). The reaction capability of such a carbocation upon interaction with organomagnesium compounds decreases [9].

The special characteristics of the behaviour of α-monosubstituted β-dicarbonyl compounds toward Grignard reagents must be considered as a particular case of heterolysis of C_α–C_β bond: $R_2{}^{\alpha}CH$–${}^{\beta}CHX_2$.

The sufficiently acceptive nature of X_2 leads to polarization of C_α–C_β bonds. The degree of polarization and the stability of the enolate formed correlate to the value of pK_a of the corresponding proton analog $HCHX_2$. On the other hand, the ability of R_2CH group to form stable carbocations corresponds to the value of pK_{R^+}, where $R^+ = R_2CH^+$.

In the examples discussed, pK_a values of unsubstituted β-dicarbonyl compounds are 10^{-9}, 10^{-10} and 10^{-14} for acetylacetone, acetoacetic and malonic esters, respectively [10]. The pK_{R^+} values vary from −13.6 for the benzhydryl carbocation to +5.61 for its bis(*p*-dimethylamino)-substituted form [11]. A similar effect of the α- and β-moieties is the possibility of C_α–C_β-cleavage under the action of various reagents.

The C_α–C_β-cleavage of the ferrocenyl-containing α-monosubstituted β-dicarbonyl compounds, β-diketones, β-ketonic esters and β-diesters, under the action of CF_3COOH or Mg and Al halides already noted [3] is consistent with this simplified scheme. Protonation of a carbonyl group as well as coordination * (or chelation) of $MgBr_2$ or $AlCl_3$ leads to C_α–C_β-fragmentation.

A weaker Lewis acid, $MgBr_2$, cleaves β-diketones and β-ketonic esters while Grignard reagents cleave only β-diketones [3]. Increase in the pK_α value results in the possibility of C_α–C_β-cleavage even under the action of weak Lewis acids, as in the case of cleavage of bis(*p*-dimethylaminophenyl)-substituted β-dicarbonyl compounds under the action of acetic acid [8]. Cleavage of tris(*p*-dimethylaminophenyl)methylnitromethane as well as tris(*p*-dimethylaminophenyl)propionic aldehyde and its vinyl analogue under the action of carboxylic acids [12] may occur accordingly. On the other hand, rearrangement from Fc(Ph)CH-substituted dibenzoylmethane to $FcCH_2$-substituted X, the pK_{R^+} value for which is in the order of 1.5 lower than that for Fc(Ph)CH [13] leads to the situation where X does not undergo fragmentation neither under the action of PhMgBr, nor with $MgBr_2$ in ether.

Considering the duality of Grignard reagent the C_α–C_β-cleavage under the action of RMgX on β-dicarbonyl compounds should be referred to as an internally catalysed electrophilic reaction.

Experimental.

Compounds III and VIIa were obtained in yields of 61% and 82% respectively by a literature method [2].

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* Ferrocenyl-*p*-dimethylaminophenyl methyl acetone also undergoes C_α–C_β cleavage under the action of $MgBr_2$. After decomposition of the reaction mixture by PhMgBr and then by water ferrocenyl-*p*-dimethylaminodiphenylmethane has been detected in the reaction products by TLC analysis.

III; m.p. 75–76°C (heptane). Found: C, 62.25; H, 6.58; N, 2.93; Fe, 11.46. $C_{26}H_{31}O_4NFe$ calcd.: C, 62.42; H, 6.55; N, 2.93; Fe, 11.70%.

VIIa; m.p. 215°C (heptane/benzene). Found: C, 80.40; H, 6.45. $C_{32}H_{32}O_2N_2$ calcd.: C, 80.64; H, 6.77%.

X: obtained by boiling an equimolar mixture of dibenzoylmethane and $[FcCH_2N(CH_3)_3]^+I$ for 1 h in dimethylformamide. Purification performed by thin-layer chromatography. Yield 92%; m.p. 139°C (heptane/benzene). Found: C, 74.19; H, 5.40; Fe, 13.33. $C_{26}H_{22}O_2Fe$ calcd.: C, 73.94; H, 5.25; Fe, 13.22%.

Interaction of I–VI, X, XI with large excesses of PhMgBr was for 15 min in ether/benzene solution, VII–IX in tetrahydrofuran. Separation of the reaction products after decomposition of the reaction mixture by water was performed by thin-layer chromatography on SiO_2 (5/40 mk) with benzene.

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