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STERIC AND KINETIC EFFECTS OF CHANGING SOLVENT AND REAGENT IN GRIGNARD REACTIONS ON SOME 4-SUBSTITUTED CYCLOHEXANONES

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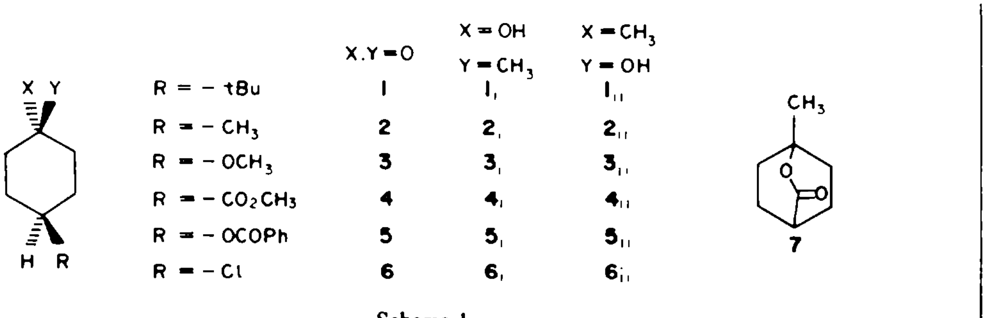
Abstract—The stereochemistry and relative rates of Grignard reactions on some 4R-substituted cyclohexanones (R = tBu, Me, OMe, CO_2Me, OCOPh and Cl) have been determined under two separate reaction conditions (MeMgI in C_6H_6 and MeMgCl in THF). The results of our studies indicate that substrates containing an ester group have a higher reaction order in Grignard reactant than other groups when reactions were carried out in the aromatic solvent. The same is not true for reactions carried out in THF. Both stereochemical product ratios and relative reaction rates are better understood assuming that compounds containing a polar group (OMe and Cl at least) react via a transition state possessing that group in the axial conformation.

APART from the 4-t-Bu and 4-Me cases very little is known about the stereochemistry and reactivity of 4-substituted cyclohexanones in Grignard reactions.

This paper describes the results we obtain for the reactions of:

(i) MeMgI in benzene at 20° and (ii) MeMgCl in THF at 20° with 4-t-Bu-(**1**), 4-Me-(**2**), 4-OMe-(**3**), 4-carbomethoxy-(**4**), 4-benzoyloxy-(**5**) and 4-chloro-cyclohexanones (**6**) (Scheme 1).

We adopted the above reaction conditions being those for which the extremes were reached in a change in stereochemistry in a preceding investigation.[1,2] We suspected they could also produce a change in mechanism.



Scheme 1.

RESULTS

Structure of reaction products. Alcohols $(\mathbf{1}\text{–}\mathbf{6})_{I}$ derive from *cis* attack of the Grignard reactant with respect to the preexisting R group, whereas alcohols $(\mathbf{1}\text{–}\mathbf{6})_{II}$ derive from *trans* attack. The alcohols arising from the reactions of Me Grignard reagents on 4-t-Bu ($\mathbf{1}_{I}$, $\mathbf{1}_{II}$)[3,4] and Me ($\mathbf{2}_{I}$, $\mathbf{2}_{II}$)[3c,4] cyclohexanone (Scheme 1) are already known.

Alcohols derived from cyclohexanones **3**,**5**, and **6** i.e. $(\mathbf{3}\text{–}\mathbf{6})_{I}$, $(\mathbf{3}\text{–}\mathbf{6})_{II}$ were separated from each other by HPLC (Experimental).

We assigned $\mathbf{3}_{I}$, $\mathbf{5}_{I}$ and $\mathbf{6}_{I}$ to alcohols with a R–C–H proton signal appearing at lower field as a single broad band as expected for a mainly equatorial proton. The same signal in compounds $\mathbf{3}_{II}$, $\mathbf{5}_{II}$ and $\mathbf{6}_{II}$ is at higher fields as a well defined multiplet in agreement with this proton being in axial conformation.

In agreement with the assigned structures the ^{13}C NMR spectra of compounds $\mathbf{3}_{I}$, $\mathbf{5}_{I}$ and $\mathbf{6}_{I}$ show the C_1 signals at lower field with respect to the same signal in the $\mathbf{3}_{II}$, $\mathbf{5}_{II}$ and $\mathbf{6}_{II}$ series.[3c,5] The reverse is true for C_2 and C_3 signals. The C_4 signal is also very diagnostic for a distinction between $\mathbf{3}_{I}$ and $\mathbf{3}_{II}$, $\mathbf{5}_{I}$ and $\mathbf{5}_{II}$ being those of the former in each couple at higher field.

The following IR spectral features confirm the above assignments: compounds $\mathbf{3}_{I}$ and $\mathbf{3}_{II}$ have in the IR a $\nu_{C\text{-}OMe}$ band at 1095 and 1110 cm^{-1}. The former is attributable to an axial OMe group† and the latter to an equatorial one.[6] Compound $\mathbf{6}_{I}$ has in the IR spectrum (CS_2) a stretching C–Cl at 710 cm^{-1} attributable to an axial Cl atom. The same band is at 760 cm^{-1} in the IR spectrum of $\mathbf{6}_{II}$ as expected for an equatorial Cl atom.[6,7] In the experimental we tabulate the complete spectral data of all compounds.

Grignard reactions of MeMgX on 4-carbomethoxy cyclohexanone (**4**) yield compounds $\mathbf{4}_{I}$, $\mathbf{4}_{II}$ and **7** whose

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†The band at 1095 cm^{-1} presents a shoulder at higher frequency which could be attributed to the equatorial conformation of the group OMe in $\mathbf{3}_{I}$.

Table 1. Stereochemistry and relative rates of Grignard reactions on 4-substituted cyclohexanones 1–6

Reaction conditions	R			1 = tBu	2 = Me	3 = OCH_3	4 = CO_2Me	5 = OCOPh	6 = Cl
	σ_I [a]			+0.016	+0.03	+0.25	+0.30	+0.469	+0.47
CH_3MgI C_6H_6 20°C	$\frac{(1\text{–}6)_{II}}{(1\text{–}6)_I}$ [b]		1	1.5	1.3	1.1	0.56	1.17	1.66
	k_{rel} [c]	set a	2	1.0	0.97	1.32	0.67	0.93	1.79
		set b	3	1.0	1.04	1.36	0.49	0.60	1.76
		set c	4	1.0	0.97	1.35	0.28	0.40	1.76
CH_3MgCl THF 20°C	$\frac{(1\text{–}6)_{II}}{(1\text{–}6)_I}$ [b]		5	2.56	2.03	0.86	1.04	1.13	1.02
	k_{rel} [c]	set a	6	1.0	0.82	1.59	1.26	1.44	2.65
		set b	7	1.0	0.82	1.58	1.36	1.56	3.13
		set c	8	1.0	0.92	1.24	1.28	1.56	2.62

a) Ref. 8

b) $\frac{4_{II} + 7}{4_I}$ in the column relative to 4-carbomethoxy cyclohexanone (4). Alcohols 4_I, 4_{II} and lactone 7 were produced in the following ratios in the two reaction conditions: $4_I/4_{II}/7$ = 64/32/4 in benzene and 49/0/51 in THF.

c) Concentrations of the added Grignard reactant: set a .4N, set b .04N, set c .02N

Mean deviation of percentage error 5%.

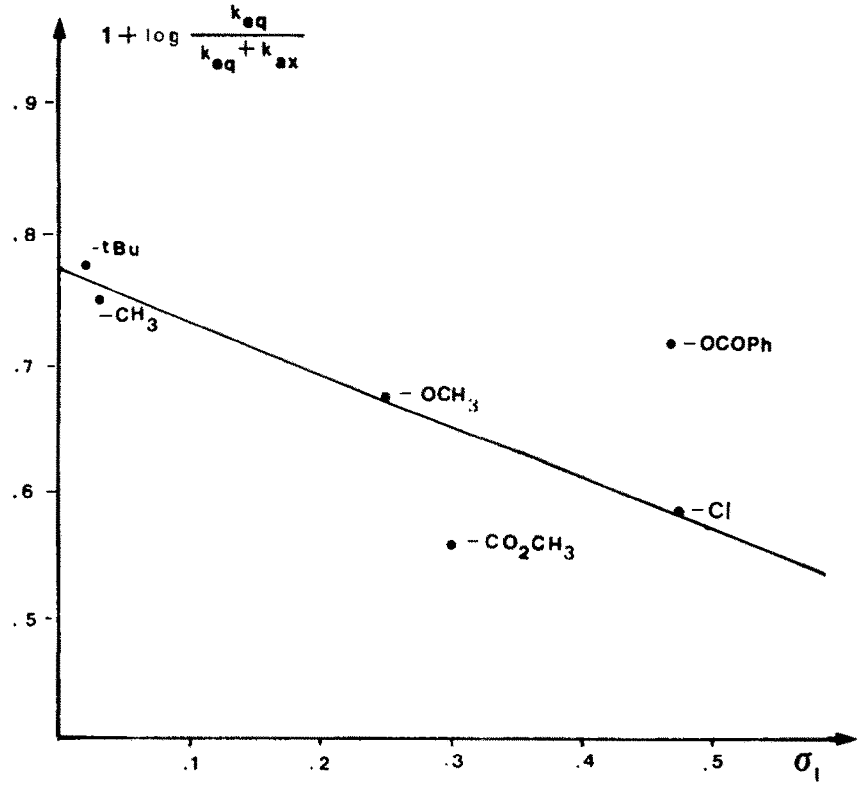

Fig. 1. Plot of $1 + \log [k_{eq}/(k_{eq} + k_{ax})]$ vs σ_I for reactions in C_6H_6 with CH_3MgI at 20°.

structures were deduced from MS, NMR and IR spectra (Experimental) and from lactone **7** which transformed into $\mathbf{4}_{II}$ upon alkaline saponification followed by esterification by diazomethane.

Compounds $\mathbf{1}_{II}$, $\mathbf{2}_{II}$, $\mathbf{3}_{I}$, $\mathbf{4}_{I}$, $\mathbf{5}_{I}$ and $\mathbf{6}_{I}$ were eluted first by GLC on PEG columns in agreement with the mostly axial conformation of the polar groups in them. Compounds $\mathbf{1}_{I}$, $\mathbf{2}_{I}$, $\mathbf{3}_{II}$, $\mathbf{4}_{II}$, $\mathbf{5}_{II}$ and $\mathbf{6}_{II}$ were eluted second.

Stereochemistry of Grignard reactions. The stereochemical results of Grignard reactions performed in accordance with the above conditions are reported in entries 1 and 5 of Table 1. It is evident from the data that no simple correlation exists between stereochemistry and electronegativity of the substituents R as represented by their Taft σ's. Among the reasons for this situation are differences in reaction mechanism, in transition state conformation and changes in the rate determining step. To throw light upon these phenomena we carried out the following kinetic measurements.

Competitive Grignard reactions. In the above reaction conditions (i) and (ii) we performed three competitive reaction sets on equimolecular mixtures of compound **4** and one of the other five compounds **1**, **2**, **3**, **5** and **6**. The three sets differed from one another in the concentration

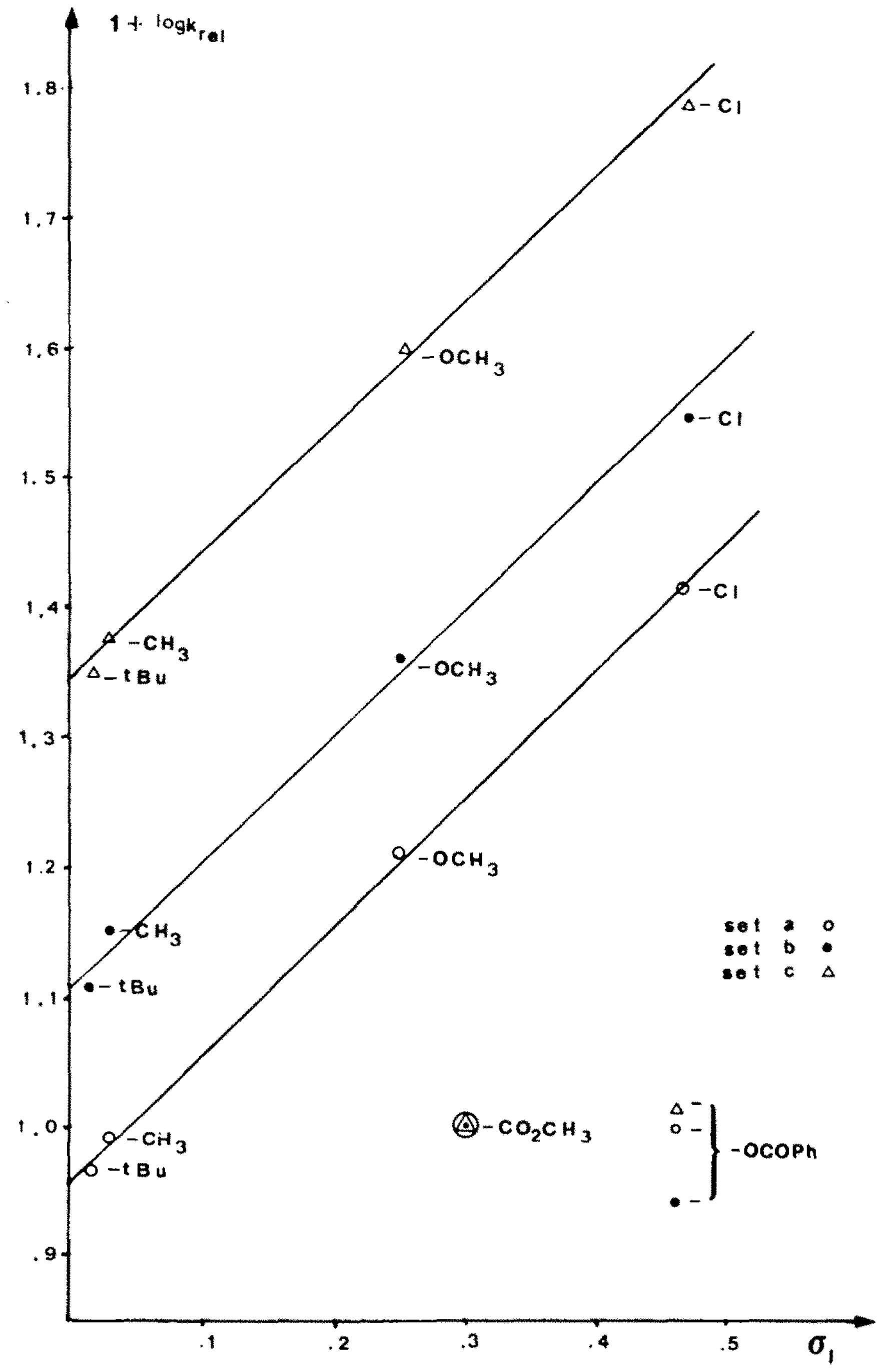

Fig. 2. Plot of 1 + log k$_{ax}$ vs σ_I for the axial attack of CH$_3$MgI in C$_6$H$_6$ at 20°.

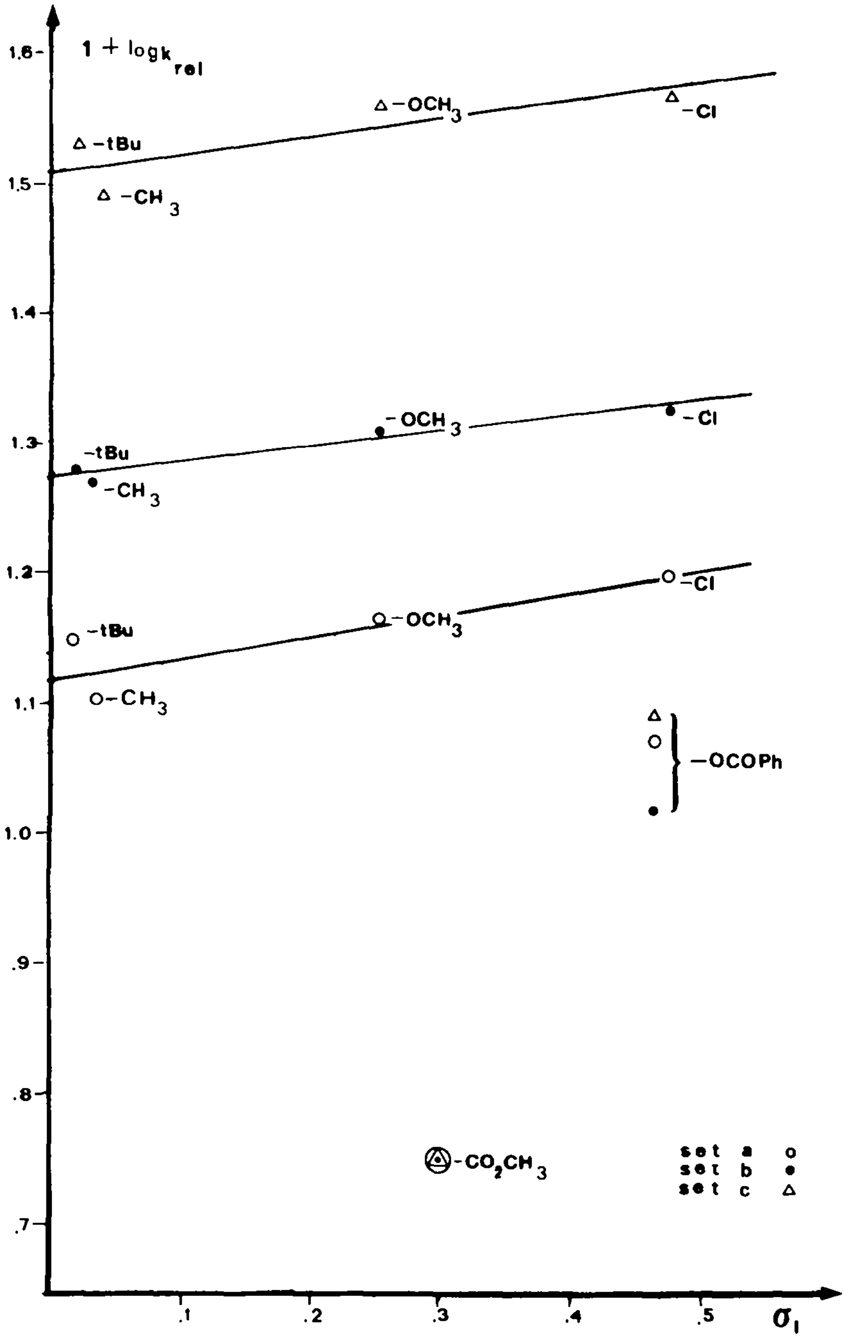

Fig. 3. Plot of 1 + log k_{eq} vs σ_I for the equatorial attack of CH_3MgI in C_6H_6 at 20°.

of the added Grignard reagent which was ≃0.4 N, ≃ 0.04 N and ≃0.02 N (sets a, b and c in Table 1).

Reaction mixtures were examined by GLC measuring the areas of the peaks corresponding to compounds **4**, $\mathbf{4}_I$, $\mathbf{4}_{II}$ and **7** on one hand, and **1**, $\mathbf{1}_I$, $\mathbf{1}_{II}$, (or **2**, $\mathbf{2}_I$, $\mathbf{2}_{II}$ and so on depending on the chosen partner for that particular experiment) on the other.

Each area was divided† by the corresponding molecular weight and the values obtained were used for calculating the yields of each competing reaction. Although reaction yields varied from run to run, the material balance (i.e. the sum of starting products and final products) was always greater than 90% of the starting material.

The relative reaction rates were calculated assuming that reactions are first order in ketone for all ketones.

Only data from reactions with yields of final products ranging from 20 to 80% were used to compute rates relative to that of compound **1** and are reported in Table 1 (entries 2, 3 and 4 for reactions in benzene and in entries 6, 7 and 8 for reactions in THF respectively). In the above entries each figure represents the mean value of at least three separate experiments.

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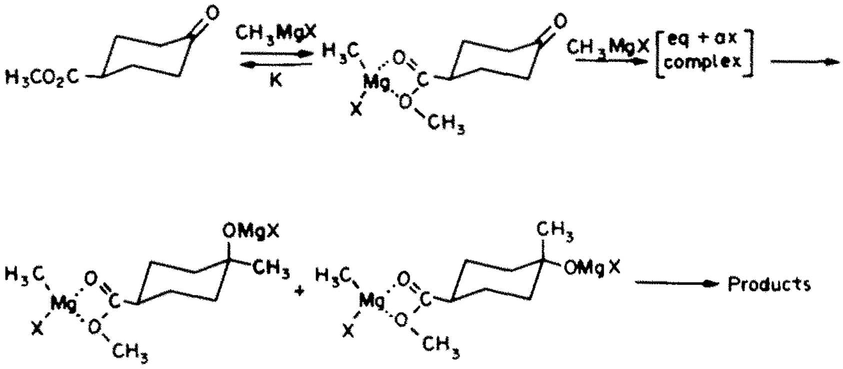
†Preliminary experiments showed that GLC responses of each of compounds (**1**–**6**) on one hand and the products of their Grignard reactions on the other, were very close to each other. Thus no correction was introduced at this point.

DISCUSSION

(1) Table 1 shows that, for reactions performed in benzene, relative rates of compounds **1**–**3** and **6** are fairly independent of the concentration of the added Grignard reactant (compare k_{rel} in entries 2, 3 and 4) whereas for compounds **4** and **5** a systematic decrease in the relative rates is observed as the concentration of the added Grignard reagent is decreased. The results indicate that the Grignard reactions of the two ketoesters have a reaction order in Grignard reactant higher than compounds **1**–**3** and **6**.

Since for compounds **4** and **5** no variations in the stereochemical product ratios were observed as the concentration of the Grignard reactant was changed, it might be inferred that the molecule (or molecules) of Mg compounds that make up the difference in order for compounds **4** and **5** doesn't discriminate between the *cis* and the *trans* side of the substrate. We believe that a possible explanation for this could be that a Grignard reagent molecule is complexed by an ester group in an unproductive fast equilibrium having a large K preceding the reaction at the ketonic function as depicted in the following equation:



Scheme 2.

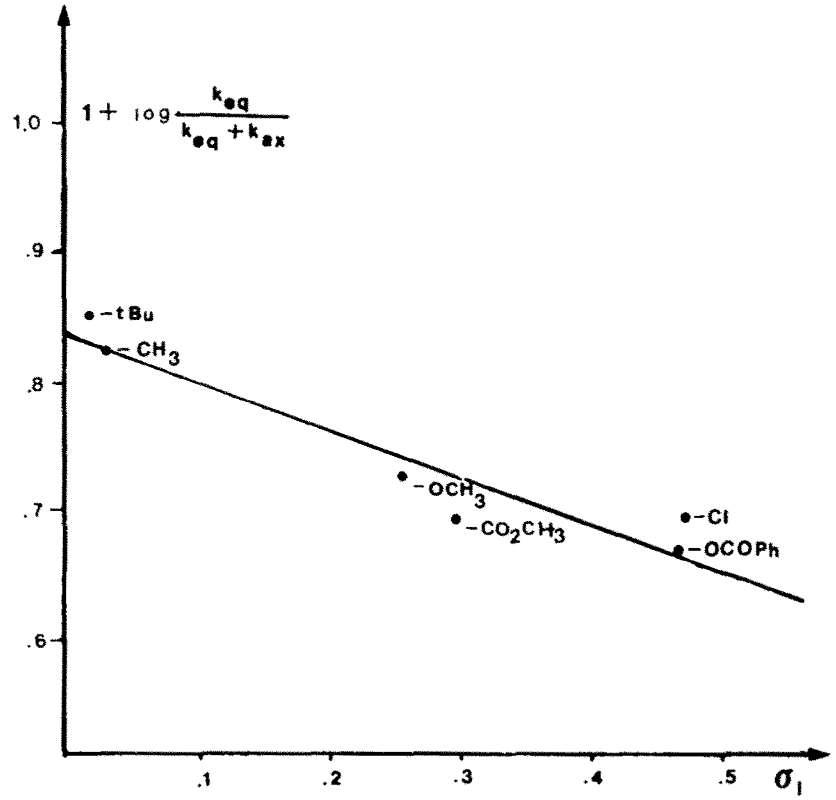


Fig. 4. Plot of $1 + \log[k_{eq}/(k_{eq} + k_{ax})]$ vs σ_I for reactions in THF with CH_3MgCl at 20°.

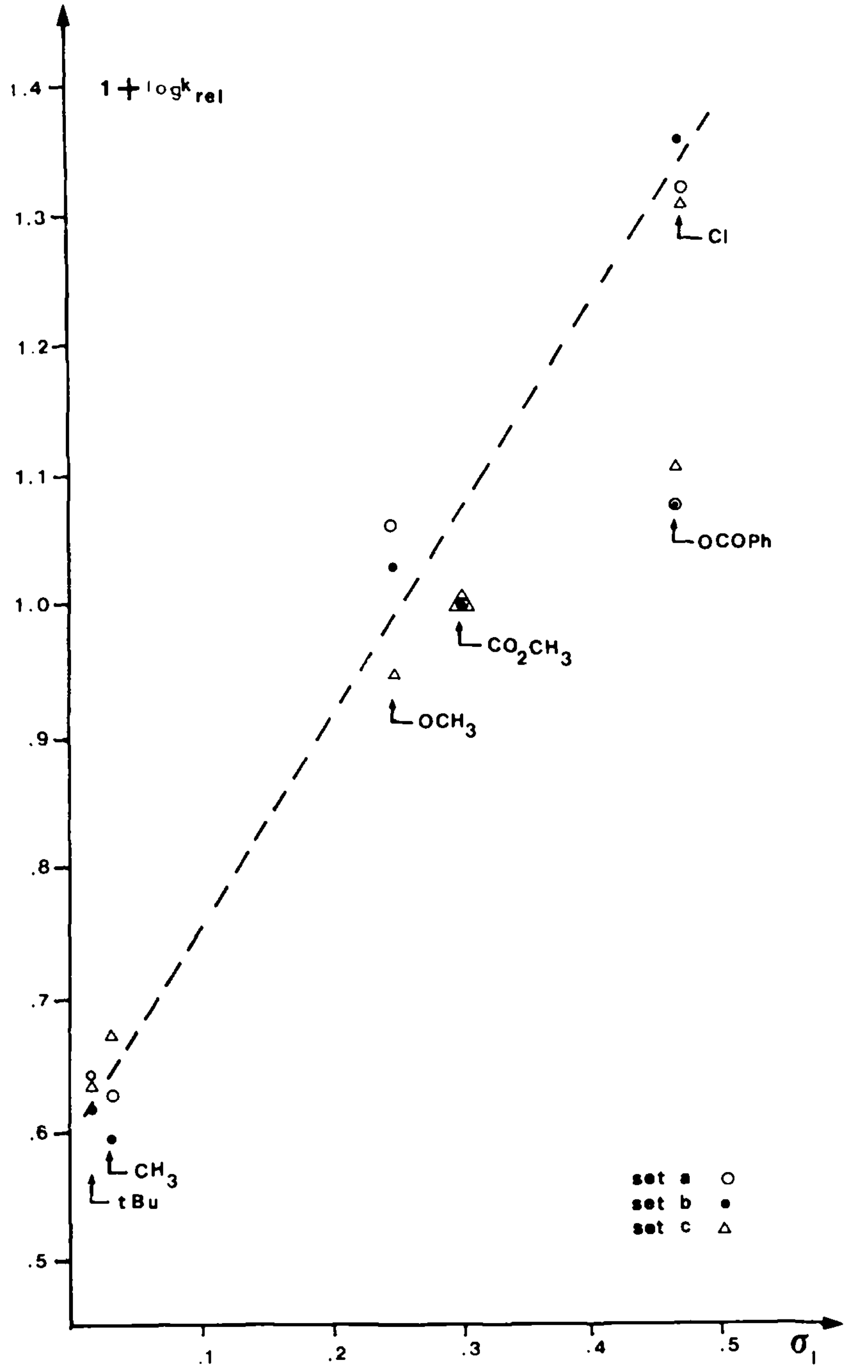


Fig. 5. Plot of $1 + \log k_{ax}$ vs σ_I for the axial attack of CH_3MgCl in THF at 20°.

Thus complexation changes the nature of the ester group and consequently makes it impossible to use for them the known values for Taft's σ's.[8]

(2) As regards compounds **1–3** and **6**, all having the same reaction order, good linear free energy relationships both of the kind log isomer % vs σ_I and $\log k_{rel}$ vs σ_I are attainable from data of Table 1. This is possible both for reactions in benzene and in THF only if one takes for compounds **3** and **6** the reciprocals of the values listed in entries 1 and 5 (Table 1). This operation is the same as admitting that compounds **3** and **6** (the ones possessing polar groups) react through transition states possessing that group in axial conformation. (Figs. 1–6).

This situation is very similar to that described by Guillerm-Drom *et al* and possibly have the origin those authors postulate.[9]

(3) It is evident from Table 1 that no systematic changes in relative reactivities were observed for reactions performed in THF as the concentration of the added Grignard reagent was changed. (Compare k_{rel} in entries 6, 7 and 8). This excludes a difference in order

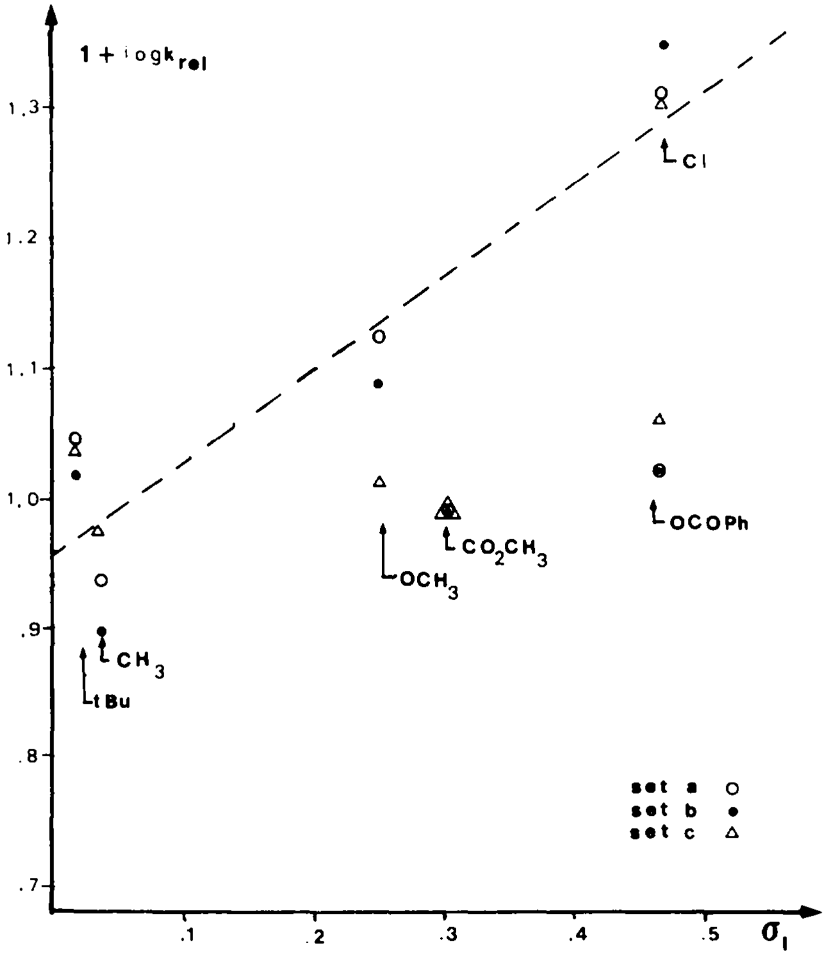


Fig. 6. Plot of $1 + \log k_{eq}$ vs σ_I for the equatorial attack of CH_3MgCl in THF at 20°.

among the various substrates and rules out for reactions in THF any complexation of the Grignard reactant by the ester groups of the kind depicted in Scheme 2.

CONCLUSIONS

The experimental data support the following conclusions:

(1) Ketoesters react with an higher order in Grignard reactant, (MeMgI), with respect to other cyclohexanones when reactions were performed in benzene.

(2) This originates from the Grignard reactant being complexed by the ester group in an early equilibrium step (Scheme 2).

(3) The complexation modifies the σ_I value of the ester group.

(4) This is not valid for reactions in THF.

(5) Transition states of reactions on 4-OMe and 4-Cl cyclohexanones have the 4-R substituent in the axial conformation both for reactions in benzene and in THF.

EXPERIMENTAL

Mps were taken on a Kofler apparatus and are uncorrected. IR spectra were recorded using a Perkin-Elmer 457 spectrometer. ^{1}H NMR spectra were recorded on a Jeol JMN-C-60 HL and on a Bruker HX 90 spectrometer.

^{13}C MR spectra were recorded on a Varian CFT 20 instrument. MS were recorded on a AEI MS 12 spectrometer: the relative intensities of the peaks (in parenthesis) are referred (Table 3) to the most intense one taken as 100%. HPLC separations were carried out on a Waters apparatus using a Microporasil 3 m 7.9 mm i.d. Waters column. Solvent hexane/EtOAc mixtures; flow = 8 ml/min. GLC analyses were carried out on a Carlo Erba Fractovap G1 apparatus using a 2 m, 2 mm i.d. glass column packed with 2% PEG 20 M on a Carbopack C, N_2 flow = 30 ml/min.

We report, in sequence, the elution order of compounds from each mixture and the most suitable temp conditions (in parenthesis T_{oven}, $T_{inj} = T_{det}$ respectively): **1**, **1**$_{II}$, **1**$_I$ (130°, 150°); **2**, **2**$_{II}$, **2**$_I$ (110°, 130°); **3**, **3**$_I$, **3**$_{II}$ (130°, 150°), **4**, **7**, **4**$_I$, **4**$_{II}$ (178°, 210°); **5**, **5**$_I$, **5**$_{II}$ (220°, 250°); **6**, **6**$_I$, **6**$_{II}$ (178°, 210°).

Starting materials. 4t-Butylcyclohexanone (Merck) had m.p. 48–49° (lit.[10], 49–50°).

Compounds **2–4** were synthesized using the method of Carlson and Zey.[11]

Compound **5** was synthesized according to Jones and Sondheimer.[12]

Compound **6** was synthesized using the method of Owen and Robins.[13]

After purification the purity of each compound was checked by GLC.

Preparations of Grignard reagents. C_6H_6 solns of MeMgI and THF solns of MeMgCl were prepared as described[2] and then diluted to the desired concentration and kept under dry N_2. Just before use, they were titrated[14] by sampling the supernatant clear soln through a rubber septum.

Isolation of products from Grignard reactions. Grignard reactions on compounds (**1–6**) were performed using standard procedure in 1 g scale in diethyl ether adding a soln of MeMgI in the

Table 2. B.p., m.p., ^{1}H NMR and ^{13}C NMR of compounds $(3\text{-}6)_I$, $(3\text{-}6)_{II}$ and 7

Compd	bp	mp	^{1}H NMR spectra: δ from TMS			^{13}C NMR spectra: δppm from TMS				
			in $CDCl_3$		in DMSO	in $CDCl_3$				
			H-C-R	Me-C-OH	Me-C-OH	C1	C2 C6	C3 C5	C4	Me
3_I	Subl 75°/ 3mm	52-54°	3.33 Broad OMe: 3.34	1.26	4.06	69.80 OMe: 55.75	34.96	26.65	76.16	29.41
3_{II}	Dist 110° 3mm	Colorless oil	3.15 Multi OMe: 3.38	1.24	4.00	68.84 OMe: 55.56	36.80	27.34	78.23	29.86
4_I	Dist 120° 20mm	Colorless oil	— CO_2Me: 3.70	1.27	4.24	69.85 CO_2Me: 51.58 C=O: 176.00	25.23	38.29	41.47	27.28
4_{II}	Subl 80°/ 1mm	57-58°	— CO_2Me: 3.72	1.26	4.01	68.57 CO_2Me: 51.60 C=O: 176.35	24.52	37.95	42.50	31.07
7	Subl 60° .2mm	64-65°	—	1.37 (CCl_4)	—	81.39 C=O: 176.98	31.36	23.76	34.87	25.52
5_I	Subl 190° 3mm	75-76 °	5.22 Broad	1.33	4.16	69.25 C=O: 165.99	34.78	26.67	70.67	30.16
5_{II}	Subl 190° 3mm	88-89°	4.98 Multi	1.28	4.19	68.71 C=O: 166.17	36.71	27.47	72.61	29.84
6_I	Subl 55° .2mm	63-64°	4.28 Broad	1.20	4.15	69.13	34.46	30.35	59.26	30.27
6_{II}	Subl 75° .2mm	92-95°	3.92 Multi	1.24	4.17	68.25	37.97	32.50	58.97	29.97

Table 3. IR, MS and C, H analyses of compounds $(\mathbf{3}\text{–}\mathbf{6})_{I}$, $(\mathbf{3}\text{–}\mathbf{6})_{II}$ and **7**

Compds.	I.R. Main vibration bands $\nu = cm^{-1}$	Mass spectrum fragmentation % base peak in parenthesis	C, H analyses
$\underline{3}_{I}$	$\nu^{CCl_4}_{Max}$: 1460w, 1450w, 1440w, 1375m, 1355w, 1250m, 1165w, 1145w, 1130w, 1095s, 1040w, 1015m, 970m, 920m, 880w.	41(11%),43(35),55(11),58(36), 67(8),68(9),69(10),71(13), 72(20),73(100),74(7),79(11), 83(8),94(11),95(12),97(33), 112(18),126(21),144(1),145(.1).	$C_8H_{16}O_2$ requires: C 66.66 H 11.11 found: C 66.28 H 11.25
$\underline{3}_{II}$	$\nu^{CCl_4}_{Max}$: 1470w, 1450w, 1375m, 1260w, 1205w, 1170m, 1140w, 1110s, 1035w, 1015w, 990w, 935m, 915m, 880w.	41(17%),43(46),55(13),58(36), 67(9),68(11),69(8),71(12), 72(20),73(100),79(13),94(14), 95(8),97(26),112(16),144(3), 145(.3).	$C_8H_{16}O_2$ requires: C 66.66 H 11.11 found: C 66.75 H 11.31
$\underline{4}_{I}$	$\nu^{CCl_4}_{Max}$: 1735s, 1465w, 1450w, 1435m, 1375m, 1340w, 1315w, 1275w, 1250m, 1205s, 1180w, 1165w, 1145s, 1105m, 1040m, 1015m, 985w, 970m, 915m, 865s.	39(13%),41(27),43(100),45(18), 55(36),58(38),59(20),67(13), 70(20),71(33),74(11),79(11), 84(46),87(82),94(14),95(61), 96(12),97(41),102(70),112(40), 125(25),140(63),141(16),144(11), 157(21),172(3.5),173(.7).	$C_9H_{16}O_3$ requires: C 62.79 H 9.30 found: C 62.52 H 9.10
$\underline{4}_{II}$	$\nu^{CCl_4}_{Max}$: 1740s, 1460w, 1450w, 1440m, 1380m, 1320m, 1260m, 1200s, 1180s, 1150s, 1100m, 1045m, 1025w, 1010w, 965m, 935w, 915m.	39(15%),41(13),43(100),44(14), 55(19),58(10),67(10),68(10), 81(31),84(44),96(25),112(17), 140(10),157(13),172(.3).	$C_9H_{16}O_3$ requires: C 62.79 H 9.30 found: C 62.61 H 9.20
$\underline{7}$	$\nu^{CCl_4}_{Max}$: 1770s, 1460w, 1385m, 1360m, 1345m, 1310w, 1290m, 1235s, 1070s, 1045m, 1020w, 960s, 920w, 880w.	39(19%),41(18),43(100),54(13), 55(26),58(11),67(11),68(13), 81(35),84(45),96(31),112(19), 140(7),141(1.2).	$C_8H_{12}O_2$ requires: C 68.57 H 8.57 found: C 68.41 H 8.71
$\underline{5}_{I}$	$\nu^{CCl_4}_{Max}$: 1720s, 1450m, 1375w, 1345w, 1315m, 1270s, 1240m, 1175m, 1110s, 1070m, 1025m, 1010m, 965m, 920m, 710s.	41(11%),43(82),58(38),69(12), 77(41),79(14),83(11),94(68), 95(12),97(34),105(100),112(79), 123(16),234(8),235(2).	$C_{14}H_{18}O_3$ requires: C 71.79 H 7.69 found: C 71.71 H 7.77
$\underline{5}_{II}$	$\nu^{CCl_4}_{Max}$: 1720s, 1450m, 1375w, 1325w, 1315m, 1275s, 1175m, 1110s, 1095m, 1070m, 1025s, 990m, 940m, 910m, 710s.	41(12%),43(83),58(33),69(11), 77(41),94(66),97(24),105(100), 112(61),123(13),234(6),235(1).	$C_{14}H_{18}O_3$ requires: C 71.79 H 7.69 found: C 71.74 H 7.60
$\underline{6}_{I}$	$\nu^{CS_2}_{Max}$: 1375m, 1270s, 1190w, 1145w, 1100m, 1000w, 970s, 910s, 760w, 740w, 710m.	43(19%),58(13),71(100),94(12), 97(13),112(12),133(13),148(2), 150(.7)..	$C_7H_{13}ClO$ requires: C 56.75 H 8.78 found C 56.86 H 8.93
$\underline{6}_{II}$	$\nu^{CS_2}_{Max}$: 1375m, 1345m, 1275m, 1265w, 1225m, 1210w, 1150m, 1095m, 1020w, 1010m, 970s, 935w, 915s, 860m, 760s, 730w, 720w.	41(11%),43(20),58(17),71(100), 94(18),97(11),112(10),133(10), 148(1),150(.3).	$C_7H_{13}ClO$ requires: C 56.75 H 8.78 found: C 56.85 H 8.85

same solvent until almost complete disappearance of starting compounds was revealed by GLC. After working up, the obtained mixtures were separated into their components by HPLC. We report, in sequence, the elution order of compounds from each mixture and (in parenthesis) the most suitable solvent (hexane/EtOAc) composition: $\mathbf{1}$, $\mathbf{1}_{II}$, $\mathbf{1}_{I}$ (80/20); $\mathbf{2}$, $\mathbf{2}_{II}$, $\mathbf{2}_{I}$ (80/20); $\mathbf{3}$, $\mathbf{3}_{I}$, $\mathbf{3}_{II}$ (70/30); $\mathbf{4}$, $\mathbf{7}$, $\mathbf{4}_{II}$, $\mathbf{4}_{I}$ (67/33); $\mathbf{5}$, $\mathbf{5}_{II}$, $\mathbf{5}_{I}$ (50/50); $\mathbf{6}$, $\mathbf{6}_{II}$, $\mathbf{6}_{I}$ (70/30).

Tables 2 and 3 report the spectral characteristics of compounds $(\mathbf{3}\text{–}\mathbf{6})_{I,II}$ and lactone **7**.

Alcohol $\mathbf{4}_{II}$ *from lactone* **7**. A soln of 0.12 g of **7** in 12 ml MeOH and 12 ml 40% W/vol KOH was refluxed during 30 min. The mixture was cooled and 20 ml of sat NH_4Cl aq was added. This soln was acidified to Congo Red with 2 N HCl and rapidly extracted with Et_2O. Ethereal solns were collected, dried over Na_2SO_4, filtered, treated with a slight excess of an ethereal soln of diazomethane and evaporated to dryness. The residue contained compound $\mathbf{4}_{II}$ and **7** as shown by GLC examination.

Competition reactions on compounds (**1**–**6**). Five 50 ml flasks were equipped with magnetic stirrer and connected by means of a five-point star-rotating receiver to a graduated burette, a condenser, gas inlet and $CaCl_2$ tube. An external heating bath maintained the temp at 20°.

The apparatus was carefully dried by flaming it under a N_2 flow. Each flask contained an equimolecular mixture of **4** with **1**–**3**, **5** and **6** respectively (0.4 mmol in all) dissolved in 4 ml of anhyd THF (or benzene). The graduated burette was filled with the suitable Grignard reaction soln which was pumped from a stock reservoir. The stoichiometric amounts of Grignard reactant were rapidly added to the mixtures while vigorous stirring was achieved by a suitable rotating apparatus. Reactions were stopped after 30 min by hydrolysis with sat NH_4Cl aq and extracted into diethyl ether. The ethereal extracts, dried over $NaSO_4$ and rectified, were examined by GLC and the areas of products (**1**–**6**), $(\mathbf{1}\text{–}\mathbf{6})_{I}$, $(\mathbf{1}\text{–}\mathbf{6})_{II}$ and **7** were measured.

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