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STERIC AND KINETIC EFFECTS OF CHANGING SOLVENT AND REACTANT IN GRIGNARD REACTIONS

CONFORMATIONALLY MOBILE VERSUS RIGID δ-KETO ESTERS†

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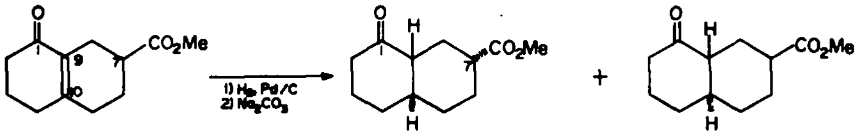
Abstract—*trans*-7α-carbomethoxy-decal-1-one (**2**) yields a mixture of the two oxy-esters **6** and **7** on reacting with MeMgX. Ratios **6**/**7** were measured for reactions performed in benzene (with X = I) and in THF (with X = Cl). The small variations of the ratios **6**/**7** as compared to those obtained in analogous experiments performed with methyl (2-oxo-cyclohexyl)-propionate (**4**) and methyl 4-methyl-5-oxo-hexanoate (**5**) suggest that conformational mobility plays a fundamental role in determining the variations of stereospecificity with varying the reaction conditions. Competitive Grignard reactions among **2**, **4** and **5** show that their reactivities are in the order **4** > **2** > **5** ($k_4/k_2 = 1.7$; $k_5/k_2 = 0.8$) when reactions are performed in benzene with X = I and **2** > **4** > **5** ($k_4/k_2 = 0.56$; $k_5/k_2 = 0.25$) when reactions are performed in THF with X = Cl. The experimental data are interpreted in terms of anchimeric assistance given by the ester group to the reactions of the keto group in conformationally mobile δ-keto esters. The occurrence of this effect depends on the reaction conditions which can favour, or not, folded transition states.

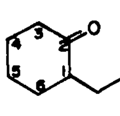
Previous publications[1-3] show that Grignard reactions on δ-keto esters can exhibit unusual changes in stereospecificity and steric direction with changing reaction conditions (reactant, solvent, temperature). We discussed the hypothesis that these variations have to be related to the conformational mobility of the two groups (the ester and the keto group) with respect to each other. In this hypothesis changes in the reaction conditions are no longer expected to produce large changes in stereospecificity with conformationally rigid δ-keto esters. Also we were convinced that changes in stereospecificity with changing reaction conditions, have to be accompanied by measurable kinetic effects.

We chose *trans* 7α-carbomethoxy-decal-1-one (**2**) as a good model of a conformationally rigid δ-keto ester. In this paper we describe the stereochemistry of Grignard reactions on **2** and the kinetic effects of changing the reaction conditions as measured in competitive reactions among the rigid δ-keto ester **2** and the two δ-keto esters **4** and **5** which have different conformational mobilities.

Starting compounds. Substances **4** and **5** were synthesised using known methods.[4,5] *trans* 7α-Carbomethoxy-decal-1-one (**2**) was synthesised by catalytically reducing **1**.[6] This operation actually yielded a mixture of four δ-keto esters (obviously the four possible pairs of enantiomers‡)



1 **2** **3**



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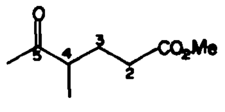

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Upon equilibration with hydroalcoholic Na_2CO_3 this mixture yielded a mixture of only **2** and **3** to which both the more stable *trans* structure at the ring junctions must be assigned. Both compounds **2** and **3**, which can be separated easily by column chromatography, are converted into a 75/25 mixture of **2** and **3** upon treatment with MeONa. Thus a suitable succession of chemical and chromatographic operations allows the transformation

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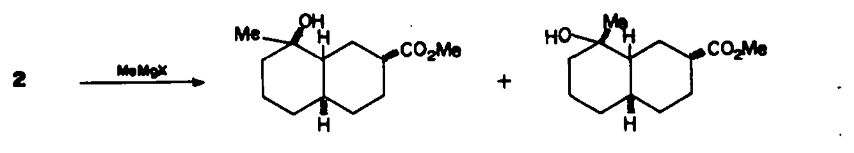
†We thank the Consiglio Nazionale delle Ricerche for financial support.

‡The freshly obtained reduction mixture contained about 26% of **2**, 2% **3** and two more keto esters (48 and 24%, respectively). We tried to separate and describe the four stereoisomers, but two of them tended to isomerize into the other two (**2** and **3**) during the manipulations or even on standing. So we gave up purifying them further.

of the reduction mixture into 2 or 3 at choice. The composition of the equilibrium mixture (2/3 = 75/25) indicates that 2 has the carbomethoxy group in the more stable equatorial conformation whereas 3 has it in the axial one. Accordingly the NMR spectrum of 3 shows the signal of the proton on C7 between 2.6δ and 2.8δ as a distinct multiplet in accordance with its equatorial conformation. The corresponding signal of compound 2 is at higher field together with the other ring proton signals (1.1δ – 2.4δ) in accordance with its axial conformation.

RESULTS

Stereochemistry of Grignard reactions on trans *7α-carbomethoxy-decal-1-one* (2). Grignard reactions on 2 yielded, as expected, mixtures of the two oxy esters 6 and 7 in which compound 6 was always largely prevailing (88–93% depending on the reaction conditions: see further)



6 7

This was shown by GLC–MS measurements on purified oxy ester fractions: these exhibit two distinct peaks both having $m/e = 226$ (Experimental; for the complete fragmentation patterns). Structure 6, with the alcoholic oxygen in the axial conformation was attributed to the compound with the lowest retention time.

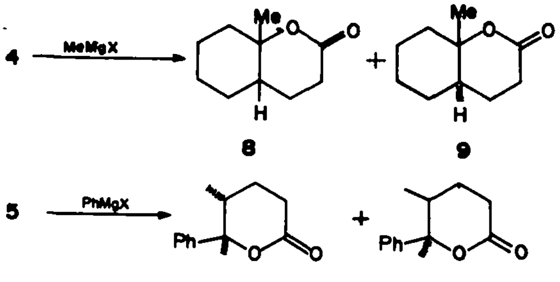
Accordingly the NMR spectra of the oxy ester fractions always show a high singlet at 1.15δ, attributable to the equatorial Me group of 6, and a small peak at 1.09δ due to the axial Me group of 7.

Grignard reactions on 2 were carried out: (a) in benzene with MeMgI at 25° and (b) in THF with MeMgCl at 60°. These conditions are those for which the extremes were reached in the change of stereospecificity for keto esters 4^1 and 5^3 (with this substrate phenyl Grignard reagents were used). In the above specified conditions 2 yields the oxy-esters 6 and 7 in the ratios as reported in Table 1, being the mean values from GLC measurements taken on several runs. Although reactions yields varied from run to run the sum 2 + 6 + 7 was always in the range 91–95% of the starting material. Table 1 also gives for comparison the ratios of lactones 8 and 9 derived from Grignard reactions on keto ester 4^1 and of lactones 10 and 11 derived from Grignard reactions on keto ester 5.^{3}

Table 1. Stereochemical product ratios for Grignard reactions of keto esters 2 and 4 with MeMgX and keto ester 5 with PhMgX

Solvent	X	Ratios		
		6/7	8/9[†]	10/11[‡]
C_6H_6	I	7.3	1.3	0.30
THF	Cl	13.5	14.4	0.48

†Ref. 1; ‡Ref. 3.



8 9 10 11

Competitive Grignard reactions between 2, 4 *and* 5. Competitive reactions were carried out on equimolecular mixtures of 2, 4 and 5 in the already specified conditions (a) and (b). Reaction mixtures were examined by GLC measuring the areas of the peaks corresponding to compounds 2, 6, 7; 4, 8, 9; and 5, 12[†]. Each area was divided by the corresponding molecular weight and the obtained values[‡] were used for calculating the yields of each competing reaction. Tables 2 and 3 give our results for competition reactions in benzene with MeMgI and in THF with MeMgCl, respectively: they are in the order of

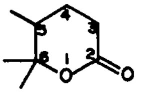


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Table 2. Rate ratios for Grignard reactions on keto esters 2, 4 and 5 with MeMgI in benzene

Run No.	Yields of reactions on:			$\frac{k_4}{k_2}$	$\frac{k_5}{k_2}$
	2	4	5		
1	1.8	2.7	1.0	1.51	0.55
2	9	11	4	1.23	0.43
3	20	28	14	1.47	0.67
4	25	43	20	1.95	0.77
5	26	43	25	1.87	0.95
6	38	61	34	1.97	0.87
7	42	64	35	1.87	0.79
8	45	60	40	1.53	0.85
9	43	71	43	2.20	1.0
10	57	78	60	1.79	1.08
11	61	82	59	1.82	0.95
12	70	89	73	1.83	1.09
13	77	87	80	1.39	1.09
		mean values		1.7 ± 0.2	0.8 ± 0.2

[†] Compound 12 is the product arising from reactions of methyl Grignard reagents on 5. See Experimental for its characterization.

[‡] GLC responses of 2, 6 and 7 were very close to each other. Thus no corrections were introduced at this point. The same is true for GLC responses of compounds 4, 8 and 9 on the one hand and 5 and 12 on the other.

Table 3. Rate ratios for Grignard reactions on keto esters 2, 4 and 5 with MeMgCl in THF

Run No.	Yields of reactions on:			$\frac{k_4}{k_2}$	$\frac{k_5}{k_2}$
	2	4	5		
1	35	21	10	0.54	0.24
2	37	24	17	0.59	0.40
3	55	35	16	0.54	0.22
4	68	47	22	0.56	0.22
5	81	59	28	0.54	0.20
6	88	71	37	0.58	0.22
		mean values		0.56 ± 0.02	0.25 ± 0.02

increasing mean yields. The values k_4/k_2 and k_5/k_2 were calculated hypothesing that reactions are of the first order for all keto esters and have the same order in Grignard reagents for all substrata. The formula $k_a/k_b = \log(a_0 - x/a_0)/\log(b_0 - y/b_0)$ in which a_0 and b_0 represent the moles of starting compounds at $t = 0$; x and y represent the moles of products was used.

DISCUSSION

The variations in ratios 6/7 (Table 1) are much smaller than those of ratios 8/9 and also smaller than those of ratios 10/11. This indicates that conformational mobility can play an important role in determining variations in stereospecificity by varying the reaction conditions in Grignard reactions. The stereospecificity we observed is very close to the findings of Suzuki *et al.*[7] in Grignard reactions on *trans* α-decalone (94.9% of the axial and 5.1% of the equatorial alcohol; ratio = 18.6), which means that the ester group of 2 has no influence on the stereospecificity of the reaction.

Competitive reactions in benzene. Keto ester 4 reacts faster than keto ester 2 ($k_4/k_2 = 1.7$) just in those conditions (reactions in benzene with MeMgI) in which it also reacts with its lowest stereospecificity (Table 1: 8/9 = 1.3 corresponding to a minimum of equatorial attack[†]). From rate ratios and stereoisomer percentages we calculated the approximate relative rate of equatorial and axial attack on 2 and 4 for reactions performed in benzene. These are reported in Fig. 1(2a and 4a) and referred to the rate of equatorial attack on 2 taken as one.

The rate of the axial attack of Grignard reagent on 4 is 6.4 times faster than in 2. This is a case of stereoselective anchimeric assistance by a remote ester group much of the same kind of that already supposed by Kwart *et al.* for both electrophilic[9] (addition of 2,4-dinitrobenzensulfenyl chloride to olefins) and nucleophilic[10] ($NaBH_4$ reductions of ketones) reactions. Also the rate exaltations are of the same order of magnitude. The only difference being that, in our case, anchimeric assistance decreases the reaction stereospecificity. The results brought us to postulate structure 13 as one of the possible[‡] transition state of Grignard reactions performed on conformationally mobile δ-keto esters in a poorly solvating medium as benzene. Structure 13 can also explain the higher reactivity of 4 with respect to 5: this one, due to the absence of the ring, has a greater freedom to rotate around the C_4-C_5 bond, and consequently it could exhibit an higher negative activation entropy.

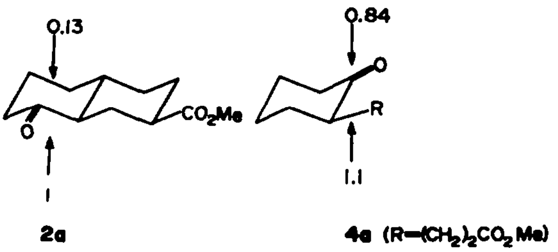
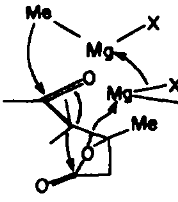


Fig. 1. Relative reaction rates of axial and equatorial attack on 2 and 4 for Grignard reactions performed in benzene with MeMgI.



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Competitive reactions in THF. Kinetic data in reactions carried out in THF with MeMgCl (Table 3: $k_4/k_2 = 0.56$; $k_5/k_2 = 0.25$) display a different situation: it is apparent that the more rigid the molecule of a δ-keto ester the higher its reactivity. In this case obviously no role can be attributed to anchimeric assistance by the ester group of 2. On the contrary, although in a high solvating medium, as THF, the two groups, with their solvent cage, tend to stay apart from each other, it is likely that the ester group might hinder the reactions at the keto group, unless they are rigidly held far from one another as in 2. This hindrance is almost random for keto ester 5 and this causes the relatively low stereospecificity of its reactions in THF (Table 1: 10/11 = 0.48). Keto ester 4, on the contrary exhibits the maximum stereospecificity (Table 1: 8/9 = 14.4) under these conditions, which implies that steric hindrance works unsymmetrically. We believe that this supports our hypothesis[3] that lactone 8, at least for reactions in THF with MeMgCl, is formed by axial attack on the axial conformation of 4: this conformation, in fact, exhibits the maximum difference in steric hindrance between the two sides of the molecule; as a consequence the reactant is forced to approach axially from the side opposite to the chain, thus justifying the lower reactivity of 4 with respect to 2. Anyway from rate ratios and stereoisomers percentages (Tables 1 and 3) it is useful to calculate the approximate relative rates of the (seeming, for 4) equatorial and axial attacks for Grignard reactions performed in THF.

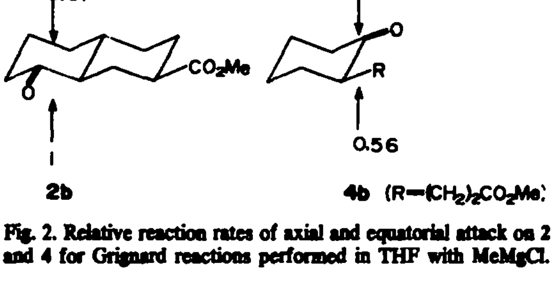

Fig. 2. Relative reaction rates of axial and equatorial attack on 2 and 4 for Grignard reactions performed in THF with MeMgCl.

[†] The normal values of equatorial/axial attack ratios for Grignard reactions on α-substituted cyclohexanones are close to 9/1.[8]

[‡] We cannot exclude that products 8 and 9 as well as 10, 11 and 12 can also be produced in parallel, anchimerically unassisted reaction.

These are reported in Fig. 2 (2b and 4b) and refer as in Fig. 1, to the rate of equatorial attack on 2 taken as one. Comparison between Figs. 1 and 2 evidence the substantial changes in the relative rates produced by changing the reactions conditions.

CONCLUSIONS

Our data indicate, that in conformationally mobile δ-keto esters, the ester group can anchimerically assist the Grignard reactions of the keto group. The occurrence of this effect depends on the reaction conditions which can favour (reactions in benzene) or not (reactions in THF) the interaction between the two functional groups through a folded transition state (like 13).

When solvation prevents anchimeric assistance, conformational mobility is, on the contrary, prejudicial to reactivity.

EXPERIMENTAL

Mps were taken on a Kofler apparatus and are uncorrected. IR Spectra were recorded using a Perkin Elmer Infracord 257 spectrophotometer. NMR spectra were recorded on a Jeol JNM-C-60 HL. MS were recorded on a AEI MS 12 spectrometer: the relative intensities of the peaks (in parenthesis) are referred to the most intense one taken as 100%. GLC-MS were recorded on the same instrument (AEI MS 12) coupled to a Varian 1400 gas chromatograph using a 2 m, 2 mm i.d. column packed with 2% OV 17 on silanized Chromosorb W, 80–100 mesh. $T_{det} = T_{inj} = 200°$; $T_{oven} = 170°$; N_2 flow = 30 ml/min. GLC analyses were carried out on a Carlo Erba Fractovap G1 apparatus using the same column and the same conditions as stated above. Alternatively a 2 m, 2 mm i.d. column packed with 0.2% PEG 20 M on Carbopack C. was used. With this last packing the GLC analysis conditions were: $T_{det} = T_{inj} = 250°$; $T_{oven} = 230°$; N_2 flow = 30 ml/min.

Starting materials. Compounds 4,[4] 5[5] and 1[6] were synthesized using the methods described. Magnesium turnings (Grignard Grade) from Carlo Erba were used.

Trans-7α-Carbomethoxy-decal-1-one (2) and *trans-7β-carbomethoxy-decal-1-one* (3). Compound 1 (1.0 g) dissolved in EtOH (100 ml) was hydrogenated over 0.5 g of 10% Pd/C at 25° and atmospheric pressure. The theoretical amount of H_2 was absorbed during 20 min. The catalyst was filtered off and the alcoholic soln was evaporated to dryness. The residue (1.0 g) was dissolved in 60 ml MeOH. This soln was refluxed with 0.6 g of Na_2CO_3 for 4 hrs and afterwards it was poured into ice-water (500 ml) and extracted several times with diethyl ether. The combined ethereal solns were dried over Na_2SO_4, filtered and evaporated to dryness. By GLC examination the residue (0.9 g) contained 69% of 2 and 31% of 3. This mixture was chromatographed on silica gel (R = 1/75) using hexane/EtOAc, 9/1 as eluant. 35 ml Fractions were collected. Fractions 16–27 (0.15 g) were pure 3; fractions 28–34 (0.1 g) contained a mixture of 2 and 3; fractions 35–60 (0.6 g) were pure 2 as white crystals.

Fractions 16–27 distilled at 75° (external temp) at 0.5 mmHg to give a colourless oil which soon crystallized, m.p. = 59–61°. NMR spectrum in CCl_4 showed the following peaks δ: 3.61(s, 3 H) attributable to the OMe group; 2.8–2.6 (m, 1H) attributable to the equatorial proton H–C–CO_2Me: 2.4–1.1 (m, 14 H).

IR spectra showed $\nu_{max}^{CCl_4}$ cm^{-1}: 3020 w, 2905 w, 2950 sh, 2920 s, 2890 sh, 2860 m, 2850 m, 1735 s, 1715 s, 1450 m, 1435 m, 1365 w, 1355 w, 1340 w, 1310 w, 1295 w, 1285 w, 1275 w, 1250 sh, 1230 sh, 1200 s, 1180 m, 1170 m, 1150 m, 1130 w, 1120 w, 1090 w, 1070 w, 1050 w, 1025 sh, 1015 w, 980 w, 960 w, 930 w, 920 w, 900 w.

MS spectrum: *m/e* 39(52%); 41(71); 50(12); 51(20); 53(27); 54(16); 55(49); 56(37); 65(20); 67(51); 77(37); 78(27); 79(88); 80(27); 81(31); 84(24); 87(18); 91(86); 93(29); 94(43); 95(20); 104(31); 105(20); 106(18); 107(22); 122(43); 132(53); 133(100); 134(31); 135(14); 150(56); 151(20); 178(23); 179(10); 192(16); 210(34); 211(5).

Found: C, 68.33; H, 8.48. $C_{12}H_{18}O_3$ requires: C, 68.55; H, 8.63%.

Fractions 35–60 after sublimation at 65° (external temp) at 0.5 mmHg had m.p. = 70–71°.

NMR spectrum in CCl_4 showed the following peaks δ: 3.60(s, 3 H) attributable to the methoxyl group; 2.3–2.1(m, 15 H).

IR spectrum showed $\nu_{max}^{CCl_4}$ cm^{-1}: 2990 w, 2950 sh, 2930 s, 2910 sh, 2860 m, 2850 m, 1740 s, 1715 s, 1460 w, 1450 m, 1435 m, 1375 w, 1340 w, 1310 w, 1280 w, 1255 m, 1230 w, 1205 w, 1165 m, 1145 w, 1115 w, 1060 sh, 1055 w, 1035 w, 1000 w, 985 w, 965 w, 910 w.

Ms spectrum: *m/e* 39(35%); 41(51); 51(12); 53(20); 54(13); 55(49); 56(41); 65(15); 67(41); 77(25); 78(20); 79(80); 80(17); 81(27); 84(12); 87(20); 91(64); 93(23); 94(37); 95(19); 104(20); 105(13); 106(21); 107(20); 122(44); 132(49); 133(100); 134(25); 150(60); 151(24); 178(32); 179(15); 192(29); 210(21); 211(4).

Found: C, 68.55; H, 8.47. $C_{12}H_{18}O_3$ requires: C, 68.55; H, 8.63%.

Equilibration experiments on 2 and 3. Metallic Na (0.01 g) was dissolved in 2 ml anhydrous MeOH. A soln of 0.05 g of pure 2(or 3) in 2 ml of the same solvent was added. The resulting soln was refluxed under anhydrous conditions for 3 hr and then poured into sat. ice-cold NH_4Cl aq. (100 ml). The water soln was extracted several times with diethyl ether. The ethereal solns were extracted with sat. $NaHCO_3$ aq., washed with water, dried over Na_2SO_4, filtered and evaporated to dryness. Yields were almost quantitative and the residues examined by GLC contained 2 and 3 in the ratio 75/25, in both the startings from pure 2 or 3.

Purification of solvents. This was done as described.[3]

Preparation of Grignard reagents was done as described.[3]

Grignard reactions on 2. All reactions were carried out under N_2. Those in benzene (with MeMgI) at 25°; those in THF (with MeMgCl) at 60°. Typically: a soln of the Grignard reagent (0.05–0.1 M; 0.4 mmol†) in the chosen solvent was added dropwise to a rapidly stirred soln of 0.063 g (0.3 mmol) of 2 dissolved in 5 ml of the same solvent.

Reactions in benzene were stopped after 10 min and those in THF after 60 min, by adding sat. NH_4Cl aq. A weighed amount of 4 was added at this point as GLC standard and the mixtures extracted with diethyl ether. The ethereal solns were washed with water, dried over Na_2SO_4, filtered and rectified. The residue was analysed by GLC to measure the total material balance 2 + 6 + 7 and the ratios 6/7.

Isolation of the oxy-esters 6 *and* 7. A Grignard reaction was performed on 2 (0.1 g) in diethyl ether with MeMgI in the usual way. Grignard reagent was added until no more 2 was present by GLC examination. The usual working up yielded a mixture of only 6 and 7 in the ratio 6/7 = 11.3 (0.1 g). This mixture distilled at 120° (external temp.) and 0.4 mmHg.

NMR spectrum in CCl_4 of the distilled mixture showed the following peaks δ: 3.61 (s, 3 H) attributable to the ester OMe group; 1.15 (s, about 3 H) which was attributed to the equatorial $\underline{Me}$–C–OH of 6 and a smaller peak (about one tenth of the 1.15δ peak) at 1.09δ which was attributed to the axial $\underline{Me}$–C–OH of 7.

GLC MS examination of the above distilled mixture permitted to record the mass spectra of both 6 and 7:

MS spectra of 6: *m/e* 39(24%); 41(45); 43(100); 45(15); 53(16); 58(13); 65(11); 67(45); 71(33); 77(20); 80(10); 81(34); 87(12); 91(43); 92(21); 93(40); 94(12); 95(15); 105(19); 106(24); 107(22); 108(19); 109(13); 119(21); 123(25); 133(38); 148(90); 149(37); 151(36); 152(13); 208(10); 211(18); 226(15); 227(4).

MS spectra of 7: *m/e* 39(38%); 41(56); 42(18); 43(100); 45(21); 50(10); 51(14); 53(20); 58(12); 65(16); 67(42); 71(34); 73(10); 77(27); 78(13); 79(49); 80(12); 81(32); 87(13); 91(51); 92(22); 93(40); 94(16); 95(15); 101(18); 105(22); 106(23); 107(21); 108(16); 109(12); 119(22); 123(19); 133(33); 148(84); 149(32); 151(20); 152(10); 158(11); 176(12); 179(14); 183(14); 208(11); 211(10); 226(10); 227(3).

IR spectra of the distilled mixture of 6 and 7 showed ν_{max}^{film} cm^{-1}: 3470 m, broad; 2920 s; 2860 m; 2840 m; 1725 s;

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†A slight excess of the Grignard reagent ensures that almost all of the starting material was consumed which improves measurement of the GLC areas of 7.

1460 sh; 1445 m; 1435 m; 1375 m; 1320 w; 1190 s; 1175 s; 1150 s; 1115 sh; 1100 m; 1085 sh; 1060 m; 1050 m; 1040 m; 1020 m; 1000 w; 970 w; 950 w; 880 m; 855 w; 830 w; 795 w; 760 m. Found: C, 69.06; H, 9.71. $C_{13}H_{22}O_3$ requires: C, 68.99; H, 9.80%.

Competition reactions. A two neck 50 ml flask was equipped with magnetic stirrer, dropping funnel, condenser, gas inlet, $CaCl_2$ tube and heating bath the temp. of which was maintained at 60° for reactions in THF and at 25° for reactions in benzene. This apparatus was carefully dried by flaming it under a dry N_2 flow. An equimolecular mixture of 2, 4 and 5 (0.9 mmol in all) dissolved in 18 ml of anhyd. THF (or benzene) was then introduced. Under vigorous stirring 10 ml of a soln 0.05 M of MeMgX (X = Cl for reactions in THF and X = I for reactions in benzene) in the chosen solvent were added dropwise during 30 min. The usual working up gave ethereal extracts which were carefully rectified. The residues were examined by GLC and the areas of 2, 6, 7; 4, 8, 9; 5 and 12 were measured.

Isolation and characterization of tetrahydro-5,6,6-trimethyl-2 H-pyran-2-one (12). Grignard reaction on 5 (0.2 g) was performed as usual in diethyl ether (25 ml). A soln of MeMgI in the same solvent was carefully added until no more 5 was present by GLC examination. Working up yielded lactone 12 (0.18 g) which was 90% pure by GLC. It was chromatographed on silica gel (R = 1/50) using $CHCl_3$/n-hexane, 2/1 as eluant. 4 ml fractions were collected. Fractions 7–12 contained pure 12 which distilled at 120–130° (external temp.) at 24 mmHg.

NMR in CCl_4 shows δ: 0.95–1.05 (d, 3 H) attributable to the Me group on C5; 1.25 (s, 3 H) and 1.38 (s, 3 H) attributable to the two Me groups on C6; 1.6–1.9 (m, 2 H) attributable to the protons on C4; 1.95–2.2 (m, about 1 H) attributable to the proton on C5; 2.25–2.55 (m, 2 H) attributable to the protons on C2.

IR spectra $\nu_{max}^{CCl_4}$ 4 cm^{-1}: 1980 m; 1940 sh; 1880 w; 1740 s; 1720 sh; 1460 w; 1420 w; 1390 w; 1370 w; 1330 w; 1270 s; 1250 w; 1210 w; 1160 w; 1135 s; 1120 m; 1080 w; 1040 m; 980 w; 905 w.

MS spectrum: *m/e* 39(39%); 41(69); 42(33); 43(100); 45(36); 55(59); 56(83); 59(55); 70(82); 74(21); 84(49); 99(52); 127(21); 142(2). Found: C, 67.41; H, 9.70. $C_8H_{14}O_2$ requires: C, 67.57; H, 9.92%.

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REFERENCES

[1] G. Di Maio, M. T. Pellegrini and P. A. Tardella, *Ric. Sci.* **38**, 234 (1968).

[2] G. Di Maio, M. T. Pellegrini and P. A. Tardella, *Ibid.* **38**, 240 (1968).

[3] A. Colantoni, G. Di Maio, C. Quagliata, E. Vecchi and E. Zeuli, *Tetrahedron* in press.

[4] G. Stork and H. K. Landesman, *J. Am. Chem. Soc.* **78**, 5128 (1956).

[5] H. E. Baumgarten and R. L. Eifert, *J. Org. Chem.* **18**, 1177 (1953).

[6] R. G. Carlson and E. G. Zey, *Ibid.* **37**, 2468 (1972).

[7] T. Suzuki, T. Kobayashi, Y. Takegamy and Y. Kawasaki, *Bull. Chem. Soc. J.* **47**, 1971 (1974).

[8] E. C. Ashby and J. T. Laemmle, *Chem. Rev.* **75**, 521–46 (1975) and refs cited.

[9] H. Kwart and L. J. Miller, *J. Am. Chem. Soc.* **83**, 4552 (1961).

[10] H. Kwart and T. Takeshita, *Ibid.* **84**, 2833 (1962).