Tetrahedron Letters No. 44, pp 4129 - 4132, 1971. Pergamon Press. Printed in Great Britain.

THE FRIEDEL CRAFTS REACTION OF ALKENONES WITH BENZENE

M.F. Ansell and S.A. Mahmud

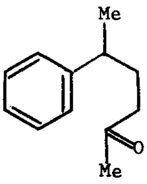
Queen Mary College (University of London)

Mile End Road, London, E.1.

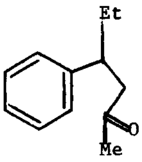
(Received in UK 29 September 1971; accepted for publication 1 October 1971)

It has been shown recently[1] that in the Friedel Craft reaction of alkenoic acids the nature of the reaction product is dependent on the relative position of the double bond and the carboxyl group. We now report a similar investigation into the Friedel Craft reaction of alkenones.

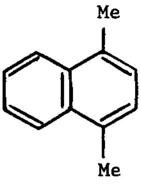
5-Phenylhexan-2-one (I) has been reported as the sole product of the reaction of benzene in the presence of aluminium chloride with either hex-3-en-2-one[2] or hex-5-en-2-one[3]. The results we have obtained from the reactions of each of the hexen-2-ones are tabulated below (Table 1). The products from these reactions were separated by g.l.c. and their structures deduced from their n.m.r. and i.r. spectra and confirmed by comparison with authentic samples.



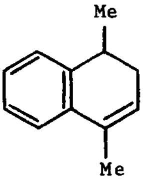
(I)



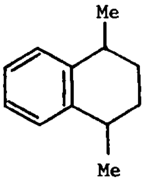
(II)



(III)



(IV)



(V)

Our results on the phenylation of hex-3-en-2-one contrast with those of Nenitzescu[2], as we find that under their conditions the major ketonic product is the 4-phenylisomer (II). We agree with Colonge[3] that 5-phenylhexan-2-one is the sole ketonic product from hex-5-en-2-one. The cyclic products, not mentioned by earlier workers, clearly arise from 5-phenylhexan-2-one which initially cyclises to 1,2-dihydro-1,4-dimethylnaphthalene (IV) which we have shown to disproportionate to the 1,4-dimethylnaphthalene (III) and the dimethyltetrahydronaphthalene (V). Such a reaction has been previously observed[4] with 4-phenylpentan-2-one. These reactions parallel those of the pentenoic acids with benzene in the presence of aluminium chloride.

Table 1. Reactions of Hexen-2-ones with Benzene/$AlCl_3$ and Related Reactions

Ketones or Related Compounds	Reaction Conditions	Recovered Hexenones	Product						
			Ketonic Products			Cyclic Products			
			% Yield	% Composition		% Yield[b]	% Composition		
				I	II		III	IV	V
Hex-3-en-2-one	A	54	10[a]	38	62	1	38	18	44
Hex-3-en-2-one	B	7	6[a]	3	97	1.5[c]	27	25	36
Hex-4-en-2-one	A		41	100	-	16.5	26	34	40
Hex-5-en-2-one	A		50	100	-	19	33	33	33
5-Phenylhexan-2-one	A		51	100	-	7.5	46	23	31
5-Phenylhexan-2-one	B		14	100	-	6	54	8	38
1,2-Dihydro-1,4-dimethyl naphthalene	A			-	-	30	15	8	77

A = 3 hr./10-20°; B = 7 hr./35-40°; a = based on unrecovered ketone;
b = based on $C_{12}H_{14}$; c = 12% product probably 1-ethyl-3-methylindene present.

The effect of the relative positions of the double bond and the carbonyl group are clearly shown in the reactions, in the presence of aluminium chloride, between benzene and hepten-2-ones and octen-2-ones to give respectively, phenylheptan-2-ones and phenyloctan-2-ones. The results of these reactions are shown in Tables 2 and 3. In these reactions, in contrast to those involving hexen-2-ones very little cyclic material is formed, although we consider the absence of 5-phenyloctan-2-one in the reaction of oct-3-en-2-one at 35-40° to be due to the removal of this product by cyclisation. Also in these reactions the 5-phenyl-isomer is not a preferred product as in the hexen-2-one reactions. The products shown in Tables 3 and 4 were isolated by preparative scale g.l.c. and identified from their i.r., n.m.r. and mass spectra.

All these results are summarised in Table 4. Clearly phenylation does not occur at the three-position as this would necessitate producing a carbonium ion adjacent to the electron attracting carbonyl group. Similarly phenylation does not occur at the terminal position since this would require the formation of a primary carbonium ion. It appears to be a general conclusion, under the reaction conditions we have used, that with straight chain $\alpha\beta$-unsaturated ketones phenylation will occur at all positions from β to ω-1 (with methyl ketones β = 4) but if the double bond is initially in the $\gamma\delta$-position (with methyl ketones 5,6-position), or more remote from the carbonyl group, phenylation will not occur closer than the δ-position (position 6- with methyl ketones). These results parallel those obtained[1] with unsaturated acids and may be rationalised in the same way in terms of steric and electronic effects.

The observed disproportionation of the dihydronaphthalene by-product referred to above probably occurs by an ionic mechanism, as is suggested by the reaction of 5-methylhex-4-en-2-one (VI) with benzene in the presence of aluminium chloride.

Table 2. Reactions of Hepten-2-ones with Benzene/$AlCl_3$

Hepten-2-one Double bond position	Reaction Conditions	Product - Phenylheptanone			
		% Yield	% Composition		
			4-Ph	5-Ph	6-Ph
(i) 3,4	A	26.1[a]	13	11	71
(ii) 3,4	B	20.0[a]	72	-	26
(iii) 4,5	A	75.0	-	11	89
(iv) Product from (iii)	B	75.0[b]	-	-	100
(v) 4,5	B	71.2[c]	-	4	94

A and B see Table 1; a = based on unrecovered ketone; b = ca. 5% 1,2-dihydro-1-methyl-4-ethylnaphthalene obtained; c = ca. 2% 1,2-dihydro-1-methyl-4-ethylnaphthalene obtained.

Table 3. Reactions of Octen-2-ones with Benzene/$AlCl_3$

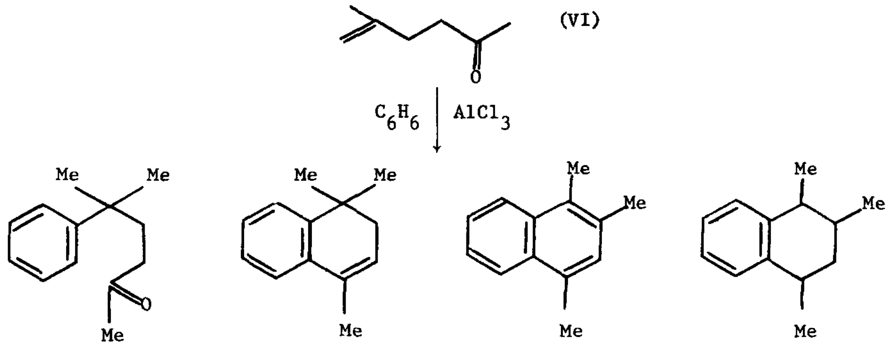
Octen-2-one Double bond position	Reaction Conditions	Product - Phenyloctan-2-one				
		% Yield	% Composition			
			4-Ph	5-Ph	6-Ph	7-Ph
3,4	A	12.5	18	7	12	62
3,4	B	27.3	56	-	13	31
4,5	A	46.4	-	8	25	67
4,5	B	46.2[a]	-	8	17	72
5.6	A	31.0	-	1	35	64
5,6	B	56.7	-	-	34	66
6,7	A	36.0	-	3	14	84
6,7	B	56.7	-	2	28	70
7,8	A	31.2[b]	-	-	6	94
7,8	B	51.6	-	-	29	71

A and B see Table 1; a = 3% ? cyclic product present; b = a high boiling product, $[C_6H_6$ + 2 x $C_8H_{14}O]$ from mass spectrum, also obtained.

Table 4. Position of phenylation of alken-2-ones

Ketone	Double bond position	Isomer obtained - Phenyl position			
Hexenone	3,4	4	5		
	4,5		5		
	5,6		5		
Heptenone	3,4	4	5		
	4,5		5	6	
Octenone	3,4	4	5	6	7
	4,5		5	6	7
	5,6		a	6	7
	6,7		a	6	7
	7,8			6	7

a = trace of 5



(VI)

46.5% (VII) 23% (VIII) 18% (IX) 12.5% (X)

The sole ketonic product was, as expected 5-methyl-5-phenylhexan-2-one (VII) which was accompanied by 1,1,4-trimethyl-1,2-dihydronaphthalene (VIII). The latter rearranges and disproportionates to 1,2,4-trimethylnaphthalene (IX) and its 1,2,3,4-tetrahydroderivative (X). The occurrance of this rearrangement suggests that the disproportionation reaction proceeds by an ionic mechanism.

In all cases gas chromatographically pure ketones were used, these being prepared either by published method or by the action of methyllithium on the corresponding acid under carefully controlled conditions. This method was found to be very convenient, especially for the preparation of αβ- and βγ-unsaturated ketones.

REFERENCES

[1] M.F. Ansell and G.F. Whitfield, J. Chem. Soc. (C), 1971, 1098.

[2] C.D. Nenitzescu and I.G. Gavat, Ann., 1935, 519, 260.

[3] J. Colonge and L. Pichat, Bull. Soc. Chim. France, 1949, 853.

[4] J.P. Quillet and J. Dreux, Bull. Soc. Chim. France, 1966, 645.