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MODERN FRIEDEL-CRAFTS CHEMISTRY. XXIII CYCLIALKYLATION BEHAVIOUR OF SOME β-PHENYLETHYL-CONTAINING CARBINOLS UNDER THE INFLUENCE OF ACID CATALYSTS

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Abstract Eleven Carbinols of general formula $PhCH_2CH_2CH(OH)R^1R^2$ (R^1=H, CH_3, C_2H_5, CH_2Ph; R^2=Ph, p-$CH_3OC_6H_4$, 1-$C_{10}H_7$, $PhCH_2$, 2$C_{10}H_7$, 2-C_4H_3S, 2-C_4H_3O) were prepared and their behaviours under the influence of $AlCl_3$, $AlCl_3$-CH_3NO_2, 85% H_2SO_4, PPA, $NaHSO_4$ and/or K10 montmorillonite were investigated. The products resulting from cyclisation, elimination and/or polymerisation were identified by both chromatographic and spectroscopic techniques. Interpretation of the results in terms of carbocation transformations and steric interactions was presented.

Introduction

As part of our on-going interest on the synthetic potentialities and mechanistic interpretations of Friedel-Crafts cyclialkylation reactions[1-20] we have undertaken the syntheses of ten mostly new arylalkanols (namely, 1a-K) with the aim of testing their cyclialkylation behaviours under various Friedel-Crafts conditions. This paper describes the results of these testings, offers plausible mechanisms to explain them and correlates them with earlier related results in the series.

Results and Discussion

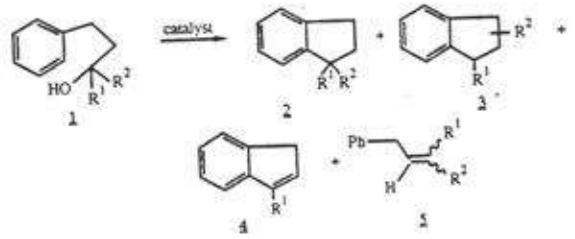
The general route chosen for the syntheses of starting arylalkanols 1a-k is formulated in equation 1 (Table-1). Meanwhile, the results of their treatment under various Friedel-Crafts conditions, as determined from combined chromatographic (TLC,GC,GC-MS) and spectroscopic data (IR, ^{1}HNMR), are depicted in Tables 2 and 3.

Examination of Table-1 reveals that the carbinols 1a-k can be sorted out into two distict types based on their experimental behaviour under the applied Friedel-Crafts conditions: (1) carbinols 1a-e that proved to be capable of ring closure to indans and/or tetralins, and (2) carbinols 1f-k that failed to cyclise yeilding alkenes and/or polymers instead.

1

No.	R_1	R_2	No.	R_1	R_2
1a	CH_3	Ph	1g	CH_3	1-$C_{10}H_7$
1b	CH_3	p-$CH_3OC_6H_4$	1h	CH_3	2-C_4H_3S
1c	CH_3	2-$C_{10}H_7$	1i	CH_3	α-C_4H_3O
1d	C_2H_5	Ph	1j	H	1-$C_{10}H_7$
1e	CH_3	$PhCH_2$	1k	H	2-$C_{10}H_7$
1f	Ph	$PhCH_2$			

Of type one carbinols, 1a-c upon treatment with $AlCl_3$-CH_3NO_2, PPA, H_2SO_4, H_3PO_4 and/or K10 clay gave products consisting of varying proportions of respective 1-aryl-1-methylindan 2 (from direct cyclisation), 2-or 3-aryl-1-methylindan 3 (from subsequent dealkylation-realkylation), 3 methylindene 4 (from subsequent dealkylation) and E-and/or Z-2-aryl-4-phenyl-2-butene 5 (from elimination) in addition to presently unidentifiable components (Scheme-1, Table-3, Entries Nos. 1-11)



Series a : R^1=CH_3, R^2 = Ph; **Series b** : R^1 = CH_3, R^2 = p-$CH_3OC_6H_4$
Series c : R^1 = CH_3, R^2=2-$C_{10}H_7$

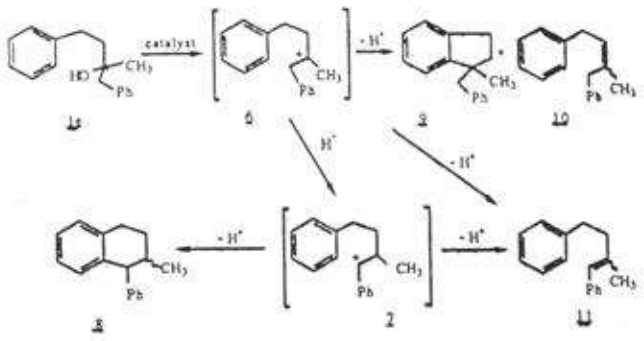
Scheme 1

The case of carbinol 1e is rather interesting. Treatment of this carbinol with $AlCl_3$, $AlCl_3$-CH_3NO_2, PPA, H_2SO_4, and H_3PO_4 gave similar products consisting

mostly of the rearranged closure product 2-methyl-1-phenyltetralin (8, mainly trans) mixed with varying proportions of the direct closure product 1-benzyl-1-methylindan 9 and the elimination products 1,4-diphenyl-2-methyl-2-butene 10 and 1,4-diphenyl-2-methyl-1-butene-11, mainly E-isomers. These results reveals that rearranged secondary benzylic carbocation closure to a 6-membered tetralin via 7 is favoured over direct ordinary tertiary carbocation closure to a 5-membered indan via 6 (Scheme-2).

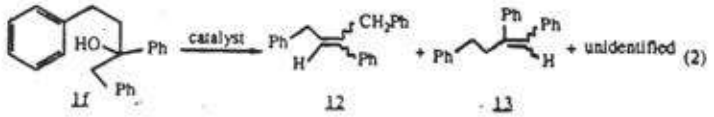
Table-1. ^{1}HNMR data of starting carbinols 1a-1k.

Comp. No.	^{1}H NMR δ ppm ($CDCl_3$)
1a	1.53 (s, 3H,CH_3), 2.13(m,2H,CH_2), 2.49(m,2H,CH_2), 2.38(bs,1H,HO) and 7.36 (m,10H,Ar-H)
1b	1,54(s,3H,CH_3), 2.16(m,2H,CH_2),2.53(m,2H,CH_2) 2.71(bs,1H,HO), 3.71 (s,3H,OCH_3), 6.83(d,2H,ArH), 7.29(m,5H,Ar-H) 7.43(d,2H,Ar-H).
1c	1.61(s,3H,CH_3), 2.36(m,2H,CH_2), 2.58(m,2H,CH_2) and 7.53 ppm (m,12H,Ar-H).
1d	1.76(t,3H,J=7HzCH_3), 1.63-2.88(m,6H,3 x CH_2), 3.18(bs,1H-OH), and 6.93-7.54 (m,10H,Ar-H)
1e	1.17(s,3H,CH_3),1.73(m,2H,CH_2) 2.31(bs,1H,HO) 2.64(m,2H,CH_2), 2.76 (s,2H,CH_2) and 7.31(m,10H,Ar-H).
1f	1.81 (bs,1H,OH), 2.23(m,2H,CH_2), 2.54(m,2H,CH_2),3.17(m,2H,3H_2) and 7.39 (m,15H,Ar-H).
1g	1.59(s,3H,CH_3), 2.43(m,4H,-CH_2CH_2-), and 7.48 (m,12H,Ar-H).
1h	1.63(s,3H,CH_3), 2.29(m,2H,CH_2), 2.67(m,2H,CH_2), 6.69(d.1H,J= 5Hz,Ar-H), and 7.23 (m,7H,Ar-H).
1i	1.53(s,3H,CH_3), 2.18(m,2H,CH_2-), 2.48(m,2H,CH_2), 6.23(m,2H,Ar-H), 7.29 (m,5H,Ar-H) and 7.36(m,1H,Ar-H).
1j	1.90(bs,1H,OH), 2.26(m,2H,CH_2) 2.83(m,2H,CH_2),5.49(t,1H, J=7Hz,CH) and 7.63 (m,12H,Ar-H).
1k	1.88(bs,1H,OH), 2.26(m,2H,CH_2), 2.76(m,2H,CH_2), 4.83(t,1H, J=7Hz,CH) and 7.58 (m,12H,Ar-H).



Scheme 2

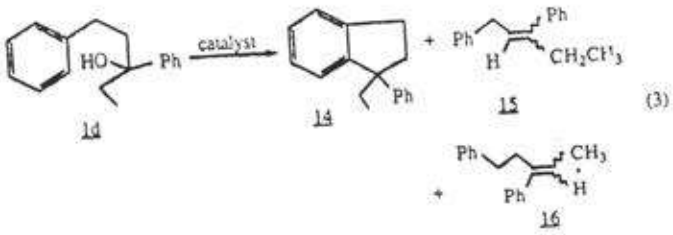
Another significant finding of this study relates to the comparative cyclialkylation behaviour of carbinols 1e and 1f in which R^1 was methyl in the former and phenyl in the latter. While 1e resulted mostly in cyclialkylation products with little elimination (Entries Nos. 12-22) (Table-3), 1f failed to do so resulting mainly in elimination to 1,2,4-tripheny1-2-butene 12 and 1,2,4-tripheny1-1-butene 13, mainly E-isomer (Table-2, Eq-2). This difference is probably due to steric factors, as the bulkier phenyl group will exert more steric strain on both the cyclialkylation intermediates and their expected products. Accordingly, elimination and/or polymerisation become the favoured reaction pathways.



(2)

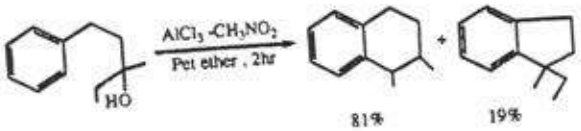
Furthermore, on comparing the results of 1e with those of the earlier data reported[15] for 1d, one striking difference can immediately be recognised. That is cyclisation to both tetralin (mainly) and indan derivatives (8 and 9, respectively) in the case of 1e but only to 1-ethyl-1-phenylindan (14, Eq. 3) in the case of 1d. As the earlier data for 1d were determined only by GC-MS, we found it essential to

affirm them also by ^1H NMR before any definitive conclusions can be drawn. Accordingly, the reaction of 1d was repeated with H_2SO_4 and further explored with $AlCl_3$ and $NaHSO_4$. The new results (Entries Nos. 24 - 26) (Table-3) while asserting the lack of tetralins in the products, revealed that the alkene fraction was a mixture of isomeric 1,3-diphenyl-2-pentenes 15 and 3,5- diphenyl-2-pentenes 16 with the E-isomers predominating (Eq. 3).



1d 14 15 16 (3)

Based on the forthgoing results, it can be concluded that direct tertiary benzylic carbocation closure to an indan is apparently favoured over rearranged ordinary secondary carbocation closure to a tertralin. That is contrary to the finding[4] that rearranged ordinary secondary carbocation closure to a tetralin is favoured over direct tertiary carbocation closure to an indan as illustrated by Eq.[4].



(4)

Turning to type (2) carbinols, it can be seen from Table-3 (Entries Nos. 27-40)

Table 2. ^{1}H NMR data of elimination and cyclisation products

Comp. No.	^{1}H NMR δ ppm ($CDCl_3$)
2a	1.16-2.87[m,4H,-(CH_2)-], 1.56(s,3H,CH_3) and 7.19 ppm (m, H,Ar-H).
2c	1.73 (s,3H,CH_3), 2.17-2.69 (m,3H,HCHCH_2],2.96(m,1H,CH), and 7.48 (m,12H,Ar-H).
Z-5a	2.10(s, 3H, CH_3), 3.34(d, 2H, J=6Hz, CH_2), 5.69(t, 1Hin J=6Hz,=CH), and 7.36 (m, 10H, Ar-H).
E-5a	2.18(s, 3H, CH_3), 3.56(d,2H, J=6Hz, CH_2), 5.69(t, 1H, J=6Hz,=CH), and 7.36 (m,10H, Ar-H).
Z-5b	2.13 (s, 3H, CH_3), 3.56(d,2H, J=6Hz,CH_2), 3.73(s,3H,OCH_3), 5.61(t,1H, J=6Hz,=CH), 6.78(d,2H, J=6Hz Ar-H), and 7.29 ppm (m, 7H, Ar-H).
E-5b	2.19(s,3H,CH_3), 3.75(d,2H, J=6Hz,CH_2) 3.88(s,3H,OCH_3), 5.89(t, 1H, J=6Hz,=CH), 6.86(d, 2H, J=6Hz Ar-H), and 7.29 (m, 7H, Ar-H)
Z-5c	2.09(s,3H,CH_3), 3.43(d,2H, J=5Hz,CH_2), 5.73(t,1H, J=5Hz, =CH), and 7.59 (m,12H,Ar-H).
E-5c	2.19(s,3H,CH_3), 3.23(d,2H, J=5Hz,CH_2), 6.15(t,1H, J=5Hz, =CH), and 7.59 (m,12H,Ar-H).
5g	2.11(s,3H,CH_3), 3.62(d,2H, J=5Hz,CH_2), 5.78(t,1H, J=5Hz, = CH), and 7.63 (m,12H,Ar-H).
E-5g	2.18(s,3H,CH_3), 3.05(d,2H,J=5Hz,CH_2), 5.85(t,1H, J=5Hz, = CH), and 7.65 (m,12H,Ar-H).
Z-5j	3.58(d,2H, J=6Hz,CH_2), 6.23(t,1H, J=Hz,=CH), and 7.69 (m, 13H, Ar-H).
E-5j	3.63(d,2H, J=6Hz,CH_2), 6.49(t,1H, J=6Hz, = CH), and 7.69 (m,13H,Ar-H).
E-5k	3.69(d,2H, J=6Hz,CH_2), 6.58(t,1H, J=6Hz, =CH), and 7.58 (m,13H,Ar-H).
8[a]	1.09(d,3H,J=5Hz, CH_3, trans-8), 1.84(d,3H, J=8Hz, CH_3, cis-8), 1.32-2.25 (complex m, 8H,2CH_2CH_2, cis-and trans-8), 3.08(m,2H,2CH-CH_3, cis-and trans-8), 3.76 (d,1H,J=5Hz, CH-Ph, trans-8), 4.19 (d,1H,J=8Hz, CH-Ph, cis-8), and 7.28 (m, 18H, Ar-H).

Table 2. Continued

E-10 1.69(s,3H,CH_3), 3.34(s,2H,CH_2PH), 3.52(d,2H, J=5Hz, CH_2Ph), 5.48(t,1H, =CH,J=5Hz), and 7.32 (m,10H, Ar-H).

E-11 1.86(s,3H,CH_2), 2.48(m, $PhCH_2CH_2$), 2.75(m,2H,$PhCH_2CH_2$), 6.26(s,1H,=CH), and 7.32 (m,10H,Ar-H).

E-12 3.68(d,2H, J=6Hz,CH_2), 4.08(s,2H,CH_2), 6.24(t,1H, J=6Hz, =CH), and 7.34 (m,15H, Ar-H).

E-13 2.83(m,2H,CH_2), 3.09(m,2H,CH_2), 6.78(s,1H,=CH), and 7.34(m,15H,Ar-H).

a These date are extracted from the nmr spectrum of the cis and trans product mixtures.

that carbinols If-k gave products resulting from elimination and/or polymerisation with none resulting from cyclisation. The failure of these carbinols to cyclise can be attributed to one or more of various factors[1-19]. Probably, it is due to steric interactions in Ig[4,5,19,20], to acid-catalysed polymerisation capabilities of thienyl and furyl moieties in Ih and Ii[21], and to a combination of carbocation stability and electrophilicity in both Ij and Ik[1,4]. In fact, it has been shown that secondary benzylic carbocations can hardly close to a five[1,17] or a seven membered ring[4]

Experimental :

General Remarks and Measurement Equipments :

These were similar to those reported in earlier papers[17,18] with the following exceptions: ^{1}H NMR spectra were sometimes recorded on a Bruker DPX-400 FT-NMR, IR spectra were recorded on a Nicolet FT-IR Spectrometer Magna 520, GC-MS data were obtained by a Shimadzu QP-5000 Mass spectrometer and Microanalyses were performed on a 2400 Perkin Elmer Series 2 CHNS Analyser.

Synthesis of Starting Carbinols. General Procedure :

Careful addition of β-phenylethyl bromide with one gram atom of Mg in dry ether) to the corresponding aldehyde or ketone (1 mole) in dry ether at ambient temperature followed by careful decomposition with saturated NH_4Cl solution, extrac-

tion with ether, washing with water, drying over anhydrous $MgSO_4$ and evaporation of solvent gave the desired carbinols in 60-80% yields ; carbinols 1a, 1b, 1d, 1f, 1h and 1i are liquids, 1e (m.p. 50), 1g (m.p. 51-52°C), 1j (m.p. 55-57°C) and 1k (m.p. 54-55°C). All of these carbinols gave correct elemental analyses (± 0.2 %). Besides their Ir spectra (film for liquids and KBr for solids) showed the characteristic OH band centered at 3420 cm^{-1} and their consistant ^1H NMR data are extracted in Table-1.

General Cyclialkylation Procedures:

The procedures described before for reactions with $AlCl_3$,[4,7] $AlCl_3/CH_3NO_2$,[4,17] PPA[17,18] and 85% H_2SO_4[4,17,19] were essentially followed. The products obtained were subjected toTLC, ^{1}HNMR, GC and in some cases also to GC-MS analyses. Combined interpretation of these data led to the results depicted in Tables 2 and 3.

Dehydration of Carbinols by $NaHSO_4$:

This was effected by heating the carbinols with $NaHSO_4$ as previously directed[17,18]. The results, as deduced from combined GC, IR and ^{1}HNMR data, are also depicted in Tables 2 and 3.

Table-3. Conditions and Results of Alkylation and Dehydration or Carbinols :

Entry No.	Arylalkanol No.	Catalyst	Reaction corldition Temp (°C)	Time (hrs)	Solvent	Observed products (%)*
1	1a	$AlCl_3/CH_3NO_2$	25	03	P.E.(40-60°C)	2a(78), 3a(10), 4a(5), unid.(07).
2		$NaHSO_4$	160	02		E-5a(80),Z-5a(20)
3	1b	$AlCl_3/CH_3NO_2$	25	03	P.E.(40-60°C)	2b(32) 3b(48), 4b(12). unid. (06).
4		H_2SO_4	25	03	CH_2Cl_2	2b(28),3b(34),4b(26). unid. (12).
5		$NaHSO_4$	160	02		E-5b (80), Z-5b (20)
6	1c	K10clay (2gm)	Reflux		P.E.(40-60°C)	2c(67), 3c(05), 4c(08). unid. (20).
7		$AlCl_3/CH_3NO_2$	25	02	P.E.(40-60°C)	2c(63),3c(23),4c(08). unid. (06).
8		H_2SO_4	160	02	CH_2Cl_2	2c(54),3c(23),4c(20). unid. (03).

Table-3. Continued

Entry No.	Arylalkanol No.	Catalyst	Reaction condition Temp (°C)	Time (hrs)	Solvent	Observed products (%)*
9		PPA	120	02		2c(71), 3c(06), 4c(09), unid. (14).
10		H_3PO_4	190	02	CH_2Cl_2	2c(86), 3c(02), 4c(04), unid. (08).
11		$NaHSO_4$	160	02		E-5c(66), Z-5c(23) unid. (08).
12	1e	$AlCl_3/CH_3NO_2$	Reflix	02	P.E.(40-60°C)	8(60), 9(15), 10(03), 11(05), unid. (17).
13		$AlCl_3/CH_3NO_2$	25	02	P.E.(40-60°C)	8(25), 9(23), 10(03), 11(05), unid. (44).
14		$AlCl_3/CH_3NO_2$	25	02	P.E.(40-60°C)	8(73), 9(10), 10(02), 11(03), unid. (12).
15		$AlCl_3/CH_3NO_2$	Reflix	45	P.E.(40-60°C)	8(78), 9(14), 10(02), unid. (03).
16		$AlCl_3/CH_3NO_2$	Reflix	02	CH_2Cl_2	8(47), 9(20), 10(02), 11(03), unid. (28).
17		$AlCl_3/CH_3NO_2$	25	20	CH_2Cl_2	8(58), 9(28), 10(02), 11(04), unid. (08).
18		$AlCl_3/CH_3NO_2$	25	20	CH_2Cl_2	8(83), 9(10), 10(02), 11(03), unid. (02).
19		$AlCl_3$	25	20	P.E.(40-60°C)	8 (19), 9(14), 10(23), 11 (14), unid. (30).
20		H_2SO_4	160	02	CH_2Cl_2	8 (15), 9 (03), 10 (19), 11 (58), unid. (05).
21		PPA	120	02		8 (64), 9(16), 10(06), 11 (09),unid. (05).
22		H_3PO_4	290	01		8 (29), 9(11), 10(19), 11 (38), unid. (03).
23		$NaHSO_4$	160	02		E-10 (34), E-11 (56). unid. (10).
24	1d	H_2SO_4	r.t.	03	CH_2Cl_2	14(49), 15 (22), 16(15), unid.(14).

Table-3. Continued

Entry No.	Arylalkanol No.	Catalyst	Reaction condition Temp (°C)	Time (hrs)	Solvent	Observed products (%)*
25		$AlCl_3$	r.t.	04	P.E. (40-60°C)	14 (24), 15(20), 16(18), unid. (38).
26		$NaHSO_4$	160	02		15(62), 16(35), unid. (03).
27	1g	$AlCl_3/CH_3NO_2$	r.t.	02	P.E. (40-60°C)	E-5g (29), Z-5g (16), polymer (26), unid (29)
28		H_2SO_4	r.t.	02	CH_2Cl_2	E-5g (32), Z-5g (21), polymer (15), unid. (32)
29		PPA	120	02		E-5g (31), Z-5g (33), polymer (23), unid. (13)
30		$NaHSO_4$	160	02		E-5g (51), Z-5g (32), unid. (17)
31	1i	$AlCl_3/CH_3NO_2$	r.t.	02	P.E. (40-60°C)	Polymer.
32		H_2SO_4	r.t.	03	CH_2Cl_2	Polymer.
33		$NaHSO_4$	160	02		Polymer
34	1h	$AlCl_3/CH_3NO_2$	r.t.	02	P.E. (40-60°C)	Polymer.
35		H_2SO_4	r.t.	02	P.E. (40-60°C)	Polymer.
36		$NaHSO_4$	160	02		Polymer.
37	1i	$AlCl_3/CH_3NO_2$	r.t.	02	P.E. (40-60°C)	Polymer.
38		$NaHSO_4$	160	02		E-5j (93), unid. (75).
39	1k	$AlCl_3/CH_3NO_2$	r.t.	02	P.E. (40-60°C)	Polymer.
40		$NaHSO_4$	160	02		E-5k (86), unid. (14).

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