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Full Paper

Friedel-Crafts chemistry. Part 55. Competing indan versus tetralin ring formations during Friedel-Crafts intramolecular cyclialkylations of some selected di-, tri- and tetraphenylated alkanols

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Abstract

Friedel-Crafts cyclialkylations of six phenylated alkanols **2a-f** to new substituted indans and tetralins mediated by $AlCl_3/CH_3NO_2$, 85% H_2SO_4 and/or PPA are described. The results revealed that competing closures of alkanols **2a-f** to structurally isomeric indan and tetralin derivatives are generally highly dependent on ring strain, carbocation stability and steric interactions but to a lesser extent on catalyst type. Unusual rearrangements from stable tertiary to less stable secondary carbocations were noted due to competing interactions. Apart from stereoisomerism (which is not the aim of this study), determination of the structural identities of the final products have constituted our main target. In practice, the structural identities of both starting materials and final products were achieved by elemental, IR, ^1H NMR and MS analyses. Mechanistic interpretations have been given in terms of carbocationic reactions and rearrangements.

Keywords: Friedel-Crafts cyclialkylation, phenylated alkanols, carbocation rearrangement, tri- and tetrasubstituted indans and tetralins.

Introduction

Indan and tetralin derivatives are a class of wide spread polycyclic aromatic hydrocarbons (PAHs) with 5- and 6-membered benzofused structures. In practice, they have occupied a unique position in the design of novel biologically active agents [1]. In nature, they are found, especially, in fossil fuels and petroleum crudes [2]. Besides, their analogues comprise the structural cores of a variety of artificial drugs [3]. They are also incorporated in more complex natural products (Fig.1) as in steroids, illudalane sesquiterpenoids and gibberellins [4].

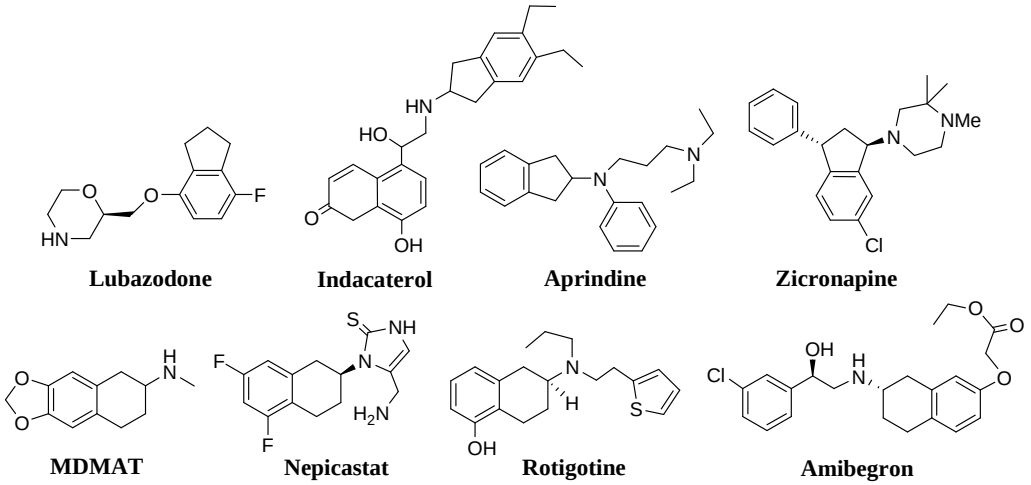


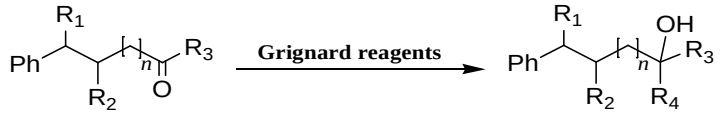
Figure 1. Examples of naturally occurring indan and tetralin derivatives.

The highly recognized industrial and biological importance of polycyclic aromatic hydrocarbons (PAHs) [5] including indans and tetralins have inspired researchers to develop facile methods for their syntheses based primarily on cyclization and cycloaddition pathways [6]. Of these methods, Friedel–Crafts reactions, Pictet–Spengler reactions, Diels–Alder reactions, photochemical rearrangements, ring-closing metathesis, transition- metal catalyzed cycloadditions, Cope rearrangements, aldol condensations, Heck-Larock ring adjustment reactions are most important [7-16]. The nature, number and relative annulations location of the benzene substituents have been shown to be the key parameters to conform before choosing a particular synthetic method [17].

In recent years, we devoted part of our research interest in Friedel-Crafts cyclialkylations to develop facile alternative routes for the building up of both novel and known carbo- and heterocyclic compounds [18-23]. In extension, we offer herein our new results about the syntheses of some novel indan and tetralin derivatives *via* competing cyclialkylations of six selected mono-, di- and triphenylated carbinols of structures **2a-f**.

Results and discussion

*Syntheses of cyclialkylating alkanols **2a-f**:* In this work, six novel substituted alkanol substrates **2a-f** were prepared smoothly by the reactions of literature known ketones and esters **1a-e** with suitable Grignard reagents. Details of these reactions are given in the experimental section and a summary of the conditions and results is depicted in Scheme 1 and in Table 1.



1a-e

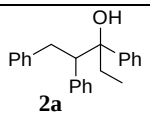
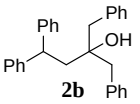
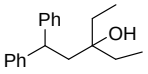
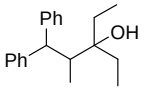
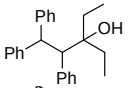
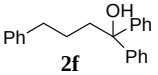
a: n = 0, R_1 = H, R_2 = R_3 = Ph
b: n = 0, R_1 = Ph, R_2 = H, R_3 = OEt
c: n = 0, R_1 = Ph, R_2 = Me, R_3 = OEt
d: n = 0, R_1 = R_2 = Ph, R_3 = OEt
e: n = 1, R_1 = R_2 = H, R_3 = OEt

2a-f

a: n = 0, R_1 = H, R_2 = R_4 = Ph, R_3 = Et,
b: n = 0, R_1 = Ph, R_2 = H, R_3 = R_4 = CH_2Ph
c: n = 0, R_1 = Ph, R_2 = H, R_3 = R_4 = Et
d: n = 0, R_1 = Ph, R_2 = Me, R_3 = R_4 = Et
e: n = 0, R_1 = R_2 = Ph, R_3 = R_4 = Et
f: n = 1, R_1 = R_2 = H, R_3 = R_4 = Ph

Scheme 1. Structures of synthesized alkanols **2a-f**.

Table 1: Summary of synthesis, results and states of required alkanols **2a-f**

No.	Substrate[Ref]	Conditions	**Mp** °C (*Refractive index*)	Product	**Yield** (%)[b]
1	**1a**[24]	EtMgBr, Et_2O, reflux, 2 hr	(1.637)	 **2a**	86.2
2	**1b**[25]	$PhCH_2MgCl$, Et_2O, rt, 20 hr	94-96	 **2b**	71.5
3	**1b**	2EtMgBr, Et_2O, rt, 10 hr	(1.5137)	 **2c**	85.7
4	**1c**	2EtMgBr, Et_2O, rt, 17 hr	(1.595)	 **2d**	85.1
5	**1d**[26]	2EtMgBr, Et_2O, rt, 20 hr	66-68	 **2e**	81.4
6	**1e**[27]	2PhMgBr, Et_2O, reflux, 3 hr	71-73[28]	 **2f**	91.8

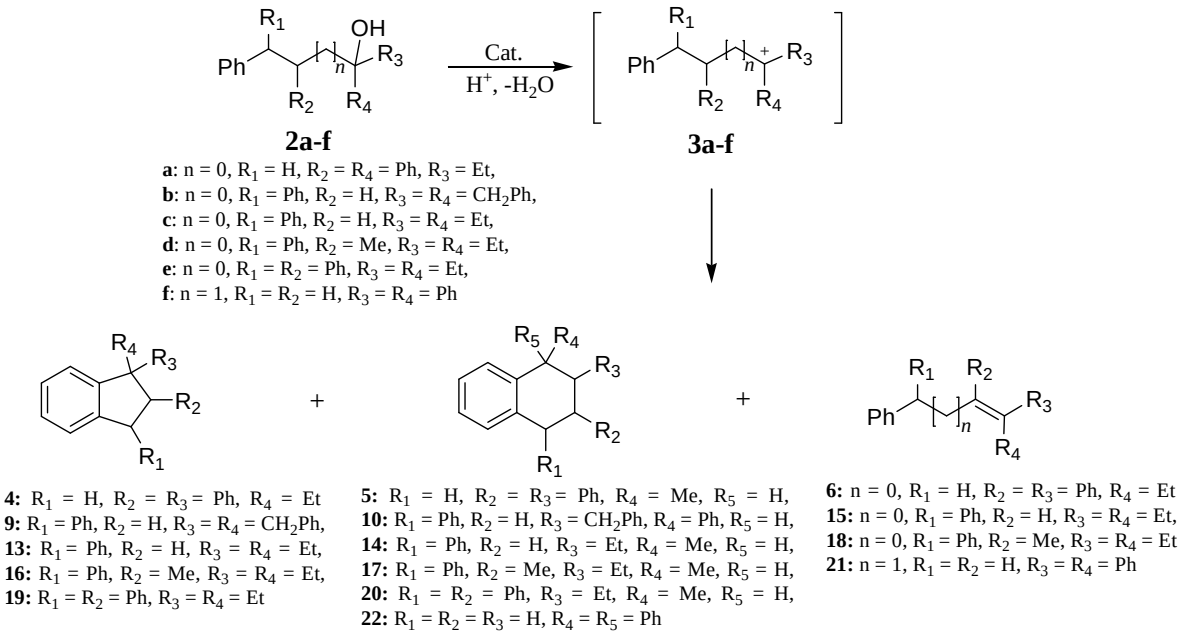
[a]All reactions were performed using 1.5 equiv. of RMgX. [i]Isolated yield.

*Cyclialkylations of alkanols **2a-f**:* Cyclialkylations of alkanols **2a-f** were carried out in the presence of $AlCl_3/CH_3NO_2$, H_2SO_4 (85%) and/or polyphosphoric acid (PPA) catalyst under varying reaction conditions. The conditions and results are depicted collectively in Scheme 2 and Table 2 and individually in Schemes 3-8. As evident, treatment of alkanols **2a-f** with acidic catalysts resulted primarily in protonation and subsequent loss of water to generate intermediate tertiary carbocations **3a-f**. Then, these carbocations were shown to undergo one or more of the following reactions: (i) ring close directly to yield alkyl/aryl-substituted indans or tetralins, (ii) rearrange to less stable secondary carbocations then close to less strained more stable tetralins, (iii) undergo elimination to alkenes and (iv) might fragment to smaller products.

*Cyclialkylation of 1,2,3-triphenylpentan-3-ol (**2a**):* Cyclialkylation of carbinol **2a** was carried out using $AlCl_3/CH_3NO_2$ catalyst. The product was shown to be a complex mixture whose GC/MS data revealed the presence of five components. Three of these (42.1%, 26%, 20.9%) have parent M^+ peaks at m/z 297 indicating isomeric relationship. The remaining minor

components (1.62% and 2.28%) showed parent M^+ peaks at m/z 118 and 180. Separation of the components by preparative thin layer chromatography and comparison of their spectra with standard ones showed the three isomers to be 1-ethyl-2,3-dihydro-1,2-diphenyl-1*H*-indene (**4**), 1,2,3,4-tetrahydro-1-methyl-2,3-diphenylnaphthalene (**5**) and *E*-1,2,3-triphenylpent-2-ene (**6**) (based on ^{1}H NMR deshielding of benzyl CH_2 by phenyl in its side). The two minor components were shown to be 1,2-diphenylethene (**7**) [resulting from fragmentation] and phenylpropene (**8**) (Table 2, Entry 1). A plausible carbocation mechanism to account for the above results is outlined in Scheme 3.

With reference to Scheme 2, two phenomena have to be emphasized: (i) the favoured formation of indan **4** over tetralin **5** could be attributed to the developing 1,2- and 1,3-steric interactions encountered in going from rearranged secondary carbocation **3a** to tetralin **5** and (ii) the stability gained in going form 5- to a 6-membered ring overpasses the stability loss in going from tertiary carbocation **3a** to rearranged secondary carbocation **3'a.** Similar phenomena were noted and reported previously by us and by other researchers.[23]



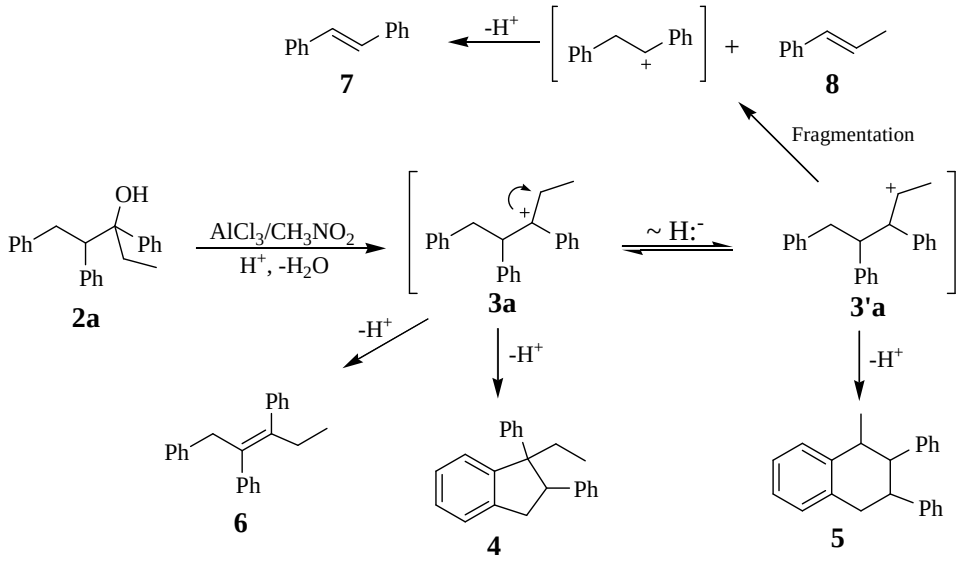
Scheme 2. Cyclialkylations of alkanols **2a-f** under Friedel-Crafts conditions**.**

Table 2: Conditions and results of Friedel-Crafts ring closures of alkanols **2a-f**

Entry	Alcohol	Reaction conditions & Yield (%)[a]	Product[Ref], Composition (%)
1	**2a**	$AlCl_3/CH_3NO_2$[b], PE[c], RT[d], 2 hr, (92.8)	**4** (42.1), **6** (26), **5** (20.9), **8** (1.62), **7** (2.28)
2	**2b**	$AlCl_3/CH_3NO_2$, PE. RT, 2 hr, (84.9)	**10** (93.36), **11** (2.3), unidentified (4.31)
3	**2b**	85% H_2SO_4[e], PE, RT, 2 hr, (82.8)	**9** (86.31), **11** (2.7), **12** (4.8)
4	**2c**	$AlCl_3/CH_3NO_2$, PE, RT, 2 hr, (92.3)	**13** (53.65), **15** (27.2), **14** (17.5)
5	**2d**	$AlCl_3/CH_3NO_2$, PE, RT, 2 hr, (83.7)	**16** (78.4), **17** (20.8)
6	**2d**	85% H_2SO_4, PE, RT, 3 hr, (86.2)	**16** (56.3), **18** (42.5)

7	**2e**	$AlCl_3/CH_3NO_2$, PE, RT, 2 hr, (80.6)	**19** (78.5), **20** (19.4)
8	**2f**	$AlCl_3/CH_3NO_2$, PE, RT, 2 hr, (84.7)	**21**[29] (100)
9	**2f**	85% H_2SO_4, PE, RT, 6 hr, (82.88)	**21** (100)
10	**2f**	PPA[f], 220-230 °C, 48 hr, (74.31)	**22**[30] (100)

[a]Isolated yield. [b]With $AlCl_3/CH_3NO_2$ catalyst reactant proportions were: carbinol (0.002 mole), $AlCl_3$ (0.0024 mole), CH_3NO_2 (0.024 mole), solvent (10 ml). [c]Petroleum ether b.p. 60-80 °C. [d]Room temperature. [e]With 85% H_2SO_4 catalyst proportions were: carbinol (0.002 mole), 85% H_2SO_4 (2 ml), solvent (10 ml/g). [f]With PPA catalyst reactant proportions were: carbinol (0.5 g) and PPA (5 g)



Scheme 3. Proposed mechanism for cyclialkylation of 1,2,3-triphenylpentan-3-ol (**2a**).

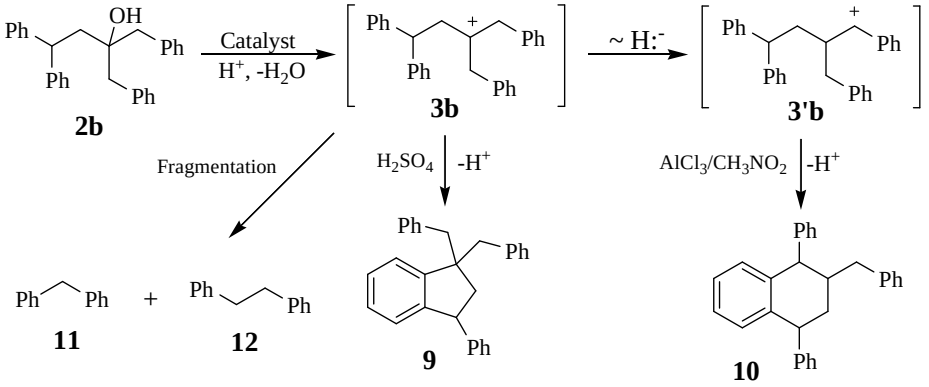
*Cyclialkylation of 2-benzyl-1,4,4-triphenylbutan-2-ol (**2b**):* Ring closure of carbinol **2b** was carried out in the presence of both $AlCl_3/CH_3NO_2$ and 85% H_2SO_4 catalysts. The major products were separated by preparative thin layer chromatography and their identities were confirmed by spectral analysis. The product with the former catalyst was shown to consist solely of 2-benzyl-1,2,3,4-tetrahydro-1,4-diphenylnaphthalene (**10**). With the latter catalyst, however, the product was shown to be 1,1-dibenzyl-2,3-dihydro-3-phenyl-1*H*-indene (**9**, 86.3%) mixed with minor amounts of diphenylmethane (**11**) and 1,2-diphenylethane (**12**) resulting from fragmentation (Scheme 4; Table 1, Entries 2 and 3).

The dominance of tertiary closure of carbocation 3b to indan 9 via reaction with sulfuric acid and of rearranged secondary closure of carbocation 3'b to tetralin 10 with aluminum chloride-nitromethane complex catalyst is due (in our view) to both catalyst size and solvation effects.

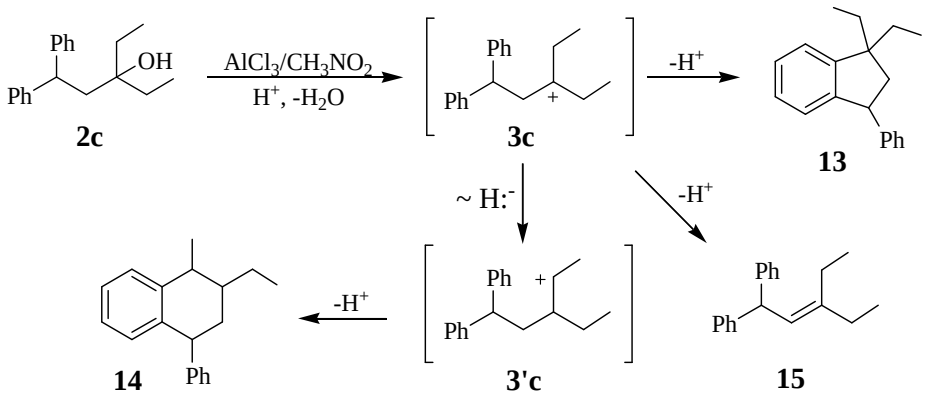
The last more sizable catalyst-complex added to solvation by nitromethane molecules of the already crowded tertiary carbocationic site will make it bulkier, less electrophilic and hence suppresses its ability to close to the already more strained five-membered indan ring. Hence closure to a 6-membered tetralin ring dominates.

*Cyclialkylation of 3-ethyl-1,1-diphenylpentan-3-ol (**2c**):* Carbinol **2c** was subjected to the action of $AlCl_3/CH_3NO_2$ for 2 hours at room temperature to give a

mixture of three components. Separation by column chromatography and analysis of spectral results showed the products to be 1,1-diethyl-2,3-dihydro-3-phenyl-1*H*-indene (**13**), 3-ethyl-1,1-diphenylpent-2-ene (**15**) and 2-ethyl-1,2,3,4-tetrahydro-1-methyl-4-phenylnaphthalene (**14**). As evident from Scheme 5, tertiary carbocation **3c** can proceed in three pathways; two leading directly to products **13** and **15** and one leading to rearranged secondary carbocation **3'c**. The latter in turn can cyclize to tetralin **14** (Scheme 5; Table 2, Entry 4).



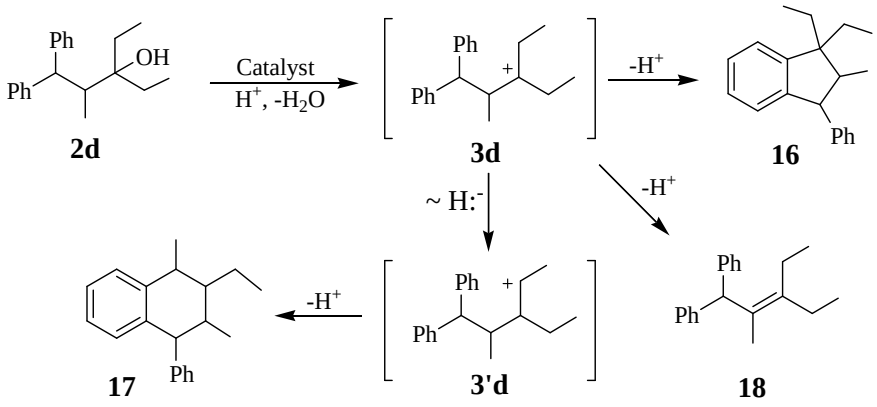
Scheme 4. Proposed mechanism for cyclialkylation of 2-benzyl-1,4,4-triphenylbutan-2-ol (**2b**).



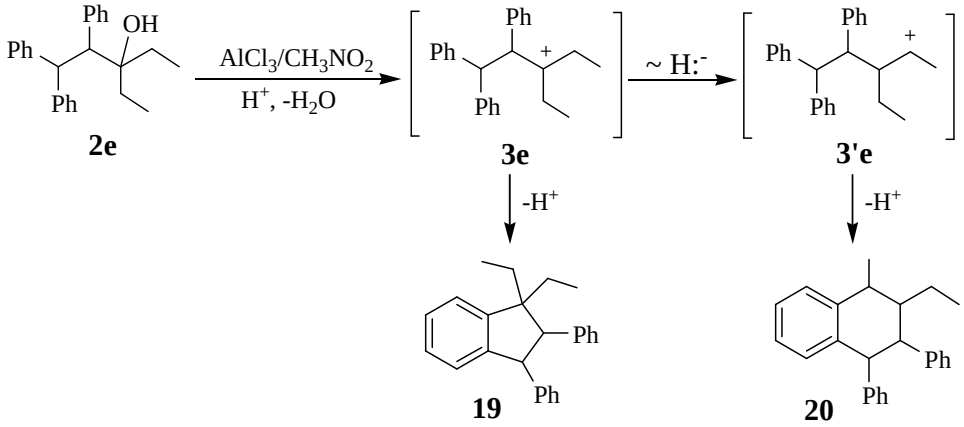
Scheme 5. Proposed mechanism for cyclialkylation of 3-ethyl-1,1-diphenylpentan-3-ol (**2c**).

Cyclialkylation of 3-ethyl-2-methyl-1,1-diphenylpentan-3-ol (2d): The cyclialkylation of this alkanol was carried out with both $AlCl_3/CH_3NO_2$ and 85% H_2SO_4 catalysts. Both products were shown by paper chromatography to be mixtures of two components. The products were separated by column chromatography and subjected to spectral and elemental analyses. Both catalysts gave 1,1-diethyl-2,3-dihydro-2-methyl-3-phenyl-1*H*-indene (**16**) as major cyclialkylation product but mixed with 2-ethyl-1,2,3,4-tetrahydro-1,3-dimethyl-4-phenylnaphthalene (**17**) in the case of $AlCl_3/CH_3NO_2$ and with 3-ethyl-2-methyl-1,1-diphenylpent-2-ene (**18**) in the case of 85% H_2SO_4 (Scheme 6; Table2, Entries 5 and 6, respectively). As shown in Scheme 6, formation of **17** resulted from rearrangement of carbocation intermediate **3d** to intermediate **3"d** before ring closure. The predominance of indan **16** as major cyclialkylation product is (in our view) due to the lesser steric interactions encountered in this compound as compared to the large 1,3- and 1,4-steric interactions

expected to occur in tetralin **17**. *Cyclialkylation of 3-ethyl-1,1,2-triphenylpentan-3-ol (**2e**):* Cyclialkylation of alkanol **2e** in the presence of $AlCl_3/CH_3NO_2$ catalyst gave a product shown by paper chromatography to consist of two products. Separation by column chromatography and analysis of spectral and elemental data showed a mixture of 1,1-diethyl-2,3-dihydro-2,3-diphenyl-1*H*-indene **(19)** and ethyl-1,2,3,4-tetrahydro-1-methyl-3,4-diphenylnaphthalene **(20)** (Scheme 7; Table2, Entry 7).



Scheme 6. Proposed mechanism for cyclialkylation of 3-ethyl-2-methyl-1,1-diphenylpentan-3-ol (**2d**).



Scheme 7. Suggested mechanism for cyclialkylation of 3-ethyl-1,1,2-triphenylpentan-3-ol (**2e**).

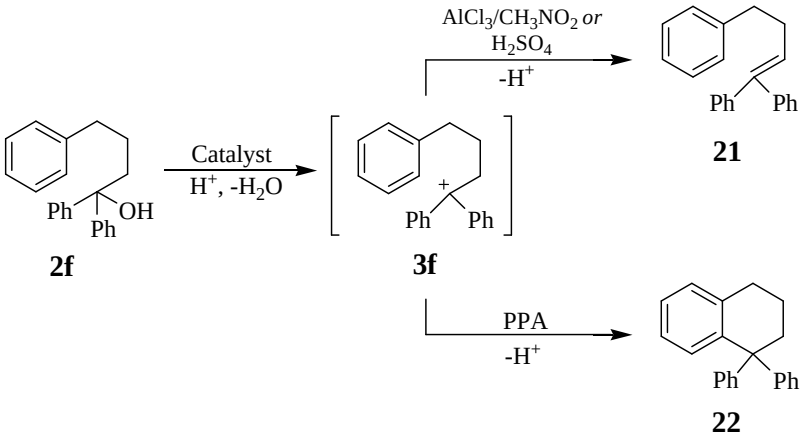
Again, as in previous case, the predominance of indan **19** as cyclialkylation product could be rationalized on steric grounds as interactions in it are expected to be much lesser than those in tetralin **20**.

*Cyclialkylation of 1,1,4 -triphenylbutan-1-ol (**2f**):* Cyclialkylation of this carbinol was carried out in the presence of $AlCl_3/CH_3NO_2$, 85% H_2SO_4 and polyphosphoric acid (PPA) catalysts. Paper chromatography indicated that all the products consisted of one component. Spectral and elemental data showed the products to be 1,1,4–triphenyl-1-butene (**21**) with the first two catalysts and 1,1-diphenyl-1,2,3,4-tetrahydrolnaphthalene (1,1-diphenyltetralin (**22**)) with PPA catalyst (Scheme 8, Table 2, Entries 8, 9 and 10).

Conclusion

In summary, a variety of newly structured indan and tetralin derivatives were made accessible through competing Friedel-Crafts ring closures of suitably synthesized mono-, di- and triphenylated alkanols. Coupled with previous findings in this

series, the results of this paper have demonstrated that the products from such reactions are highly dependent on numerous factors, most important of which are: (i) ring size or ring strain effects, (ii) steric interactions, (iii) carbocation stability at the alkyl closure site, (iv) electronic interactions in the aryl moiety and (v) reaction variables including catalyst type, temperature, time and solvent type.



Scheme 8. Suggested mechanism for cyclialkylation of 1,1,4 -triphenylbutan-1-ol (**2f**)

Experimental

Instrumentation. Melting points were measured on a digital Gallenkamp capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Shimadzo 470 Infrared spectrophotometer using KBr wafer and thin film techniques (ν cm^{-1}). ^1H NMR spectra were recorded by 90 MHz Varian ^1H NMR spectrometer using the appropriate deuteriated solvent with TMS as internal standard. Chemical shifts (δ) and *J* values are reported in ppm and Hz, respectively. Elemental analyses were performed on a Perkin-Elmer 2400 Series II analyzer. The mass spectra were performed by JEOL JMS 600 spectrometer at an ionizing potential of 70 eν using the direct inlet system. (GC/MS) was performed by GC-Hewlett Packard connected with JWS 600H using the direct inlet system. Reactions were monitored by thin layer chromatography (TLC) using precoated silica plates (Kiesel 60, F 254, E. Merck) visualized with UV light. Flash column chromatography (FC) was performed on silica gel (230-400 mesh, E. Merck). All reagents were purchased from Merck, Sigma or Aldrich Chemical Co. and were used without further purification.

General procedure for synthesis of alcohols 2a-f:

To an ice-cold Grignard reagent solution obtained from Mg turnings (0.2 g, 8 mmol), alkyl-or aryl halide (8 mmol) in ether (25 mL), was added a solution of ketone **9a,b** (6.6 mmol) or esters **11** (3.3 mmol) in ether (30 mL). The reaction mixture was stirred at required temperature for the appointed time (Table 1) followed by decomposition with *sat. aq.* NH_4Cl solution. The product was extracted with ether (3×30 mL) and the combined extracts were washed with water, dried over anhydrous Na_2SO_4 and the solvent was evaporated. The residue was purified by flash column chromatography (basic

alumina, EtOAc/*n*-hexane, 1/1) gave the pure product **12a-c**. The conditions and yields are shown in Table 1 and spectral data are given below:

1,2,3-Triphenylpentan-3-ol (2a): Colorless viscous oil: n_D^{25} 1.637, 86.2%; IR (Film) ν_{max} 3550, 3450, 3030, 2950, 1595, 1580, 1480, 1440, 1375, 1180, 1065, 1020, 740, 695 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.75 (t, 3H, *J* = 9, CH_3), 1.9 (s, 1 H, OH exchangeable with D_2O), 2.0-2.3 (q, 2 H, *J* = 6 Hz, *J* = 9 Hz, CH_2), 2.9-3.8 (m, 3H, unresolved $CHCH_2$) and 7.0-7.9 (d, 15H, ArH). Anal. Calcd. for $C_{23}H_{24}O$ (316): C, 87.34; H, 7.59. Found; C, 87.23; H, 7.51 %.

2-Benzyl-1,4,4-triphenylbutan-2-ol (2b): White crystals: m.p. 94-96 C, 76.7%; IR (KBr) ν_{max} 3540, 3010, 2920, 1590, 1480, 1440, 1350, 1250, 1070, 1020, 740, 690 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 1.3 (s, 1H, OH exchangeable with D_2O), 2.47 (d, 2H, *J* = 9 Hz, CH_2), 2.9 (s, 4H, 2 $PhCH_2$), 4.4 (t, 1H, *J* = 9 Hz, $(Ph)_2CH$) and 7.4-7.75 (d, 20H, ArH). Anal. Calcd. for $C_{29}H_{28}O$ (392): C, 88.77; H, 7.14. Found; C, 88.73; H, 7.29 %.

3-Ethyl-1,1-diphenylpentan-3-ol (2c): Colorless oil: n_D^{25} 1.5137, 85.7%; IR (Film) ν_{max} 3590, 3480, 3030, 2990, 1590, 1595, 1445, 1310, 1215, 1080, 740, 700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.7 (t, 6H, *J* = 7.5Hz, $2CH_3$), 1.4 (m, 4H, *J* = 9Hz, $2CH_2$), 1.5 (s, 1H, OH exchangeable with D_2O), 2.2 (d, 2H, *J* = 9Hz, CH_2), 4.2 (t, 1H, *J* = 9Hz, CH) and 7.1-7.4 (m, 10H, ArH). Anal. Calcd. for $C_{19}H_{24}O$ (268): C, 85.07; H, 8.95. Found: C, 85.71; H, 8.58 %.

3-Ethyl-2-methyl-1,1-diphenylpentan-3-ol (2d): Colorless viscous oil; n_D^{25} 1.595, 85.1%; IR (Film) ν_{max} 3580, 3060, 2950, 1595, 1484, 1445, 1370, 1210, 1025, 740, 695 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.7 (t, 6H, *J* = 6Hz, $2CH_3$), 0.9 (d, 3H, *J* = 6Hz, CH_3), 1.7 (s, 1H, OH exchangeable with D_2O), 2.4-2.7 (m, 1H, *J* = 9Hz, CH), 4.1 (m, 1H, *J* = 9Hz, $(Ph)_2CH$) and 6.7-7.2 (t, 10H, ArH). Anal. Calcd. for $C_{20}H_{26}O$ (282): C, 85.10; H, 9.22. Found; C, 85.37; H, 8.95 %.

3-Ethyl-1,1,2-triphenylpentan-3-ol (2e): White crystals; m.p. 66-68 °C, 81.4%; IR (KBr) ν_{max} 3570, 3460, 3050, 2975, 1590, 1540, 1490, 1445, 1340, 1180, 1115, 1065, 740, 695 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.7 (t, 6H, *J* = 6Hz, $2CH_3$), 2.0-2.5 (m, 4H, *J* = 6Hz, $2CH_2$), 3.3 (s, 1H, OH exchangeable with D_2O), 4.6 (d, 1H, *J* = 10.5Hz , PhC^2H), 4.8 (d, 1H, *J* = 10.5Hz, $(Ph)_2C^1H$) and 6.8-7.6 (m, 15H, ArH). Anal. Calcd. for $C_{25}H_{28}O$ (344): C, 87.20; H, 8.13. Found: C, 87.25; H, 8.40 %.

1,1,4-Triphenyl-1-butanol (2f): White crystals, mp 71-73 °C; IR (KBr) ν_{max} 3560, 3070, 2950, 1590, 1480, 1440, 1350, 1240, 1160, 1030, 745, 695 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 1.5 (m, 2H, *J* = 7.5 Hz, C^3H_2), 2.2 (t, 2H, *J* = 7.5 Hz, C^2H_2), 2.3 (s, 1H, OH exchangeable with D_2O), 2.5 (t, 2H, *J* = 7.5 Hz, C^4H_2), and 6.9-7.4 ppm (m, 15H, ArH).

Cyclialkylation procedures

The procedures described earlier [18] for cyclialkylation of arylalkanols with $AlCl_3/CH_3NO_2$, PPA and H_2SO_4 were essentially followed. The crude oily or solid products were purified by flash column chromatography (neutral alumina, EtOAc/*n*-hexane, 1/2) and by

crystallization from a suitable solvents for the solid products gave the pure product. The conditions and yields for the products are shown in Tables 2, while the physical constants and spectral data of the products are given in the following:

1-Ethyl-2,3-dihydro-1,2-diphenyl-1*H*-indene (4): Yellowish viscous oil: n_D^{25} 1.6109, R_f 0.53; (silica gel, *n*-hexane/AcOEt; 8.9:1.1); IR (Film) ν_{max} 3050, 2965, 1588, 1482, 1440, 1360, 1380, 1020, 743, 697 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 1.1 (t, 3H, *J* = 6 Hz, CH_3), 2.1 (q, 2H, *J* = 6Hz, CH_2), 3-3.8 (unresolved m, 3H, $CHCH_2$), 7.1-7.4 (m, 14 H, ArH). MS (EI, 70 eV) m/z (%), 297 (M^+–H, 89.1), 268 (M^+–H–C_2H_5, 100), 206 (M^+–CH_3–Ph, 94.8), 192 (M^+–C_2H_5–Ph, 21.3), 115 (M^+–C_2H_5–2Ph, 12), 91 (13.8), 90 (79.3), 77 (14.5).

1,2,3,4-Tetrahydro-1-methyl-2,3-diphenylnaphthalene (5): Yellow viscous oil; n_D^{25} 1.5639; R_f 0.64 (silica gel, *n*-hexane/AcOEt; 8.9:1.1); IR (Film) ν_{max} 3010, 3000, 2880, 1592, 1490, 1449, 1070, 1025, 740, 690 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 1.2 (d, 3H, *J* = 9Hz, CH_3), 2.4-2.8 (m, 2H, unresolved C^4H_2), 3.2-3.9 (m, 3H, unresolved C^1H-C^2H-C^3H) and 7-7.8 ppm (m, 15H, Ar). MS (EI, 70 eV) m/z (%), 297 (M^+–H, 11.8), 268 (M^+–H–C_2H_5, 37), 221 (M^+–2H–Ph, 12.9), 192 (M^+–C_2H_5–Ph, 14), 177 (56.9), 166 (98.8), 144 (M^+–2Ph, 1.5), 105 (2.8), 91 (11.1), 90 (100), 77 (12), 65 (1.1), 51 (15.4).

E-1,2,3-Triphenylpent-2-ene (6): Yellow oil: n_D^{25} 1.5937; R_f 0.42 (silica gel, *n*-hexane/AcOEt; 8.9:1.1); IR (Film) ν_{max} 3040, 2990, 1590, 1568, 1480, 1440, 1360, 1070, 1020, 750, 690 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 1.1 (t, 3H, *J* = 9Hz, CH_3), 2.5-2.9 (q, 1H, *J* = 9Hz, CH_2), 2.4 (d, 2H, *J* = 9Hz, CH_2;deshielded by phenyl group in its side), and 7.1-7.4 (d, 15H, ArH). MS (EI, 70 eV) m/z (%), 297 (M^+–H, 10.3), 280 (M^+–3H–CH_3, 39.6), 221 (M^+–Ph, 3.6), 206 (M^+–CH_3–Ph, 100), 177 (51.1), 166 (78.9), 144 (M^+–2Ph, 3.3), 129 (M^+–CH_3–2Ph, 10.8), 117 (M^+–$C_{14}H_{13}$, 99.5), 91 (10.1), 90 (89.7), 77 (12.6), 65 (11.7), 51 (15.4).

1,1-Dibenzyl-2,3-dihydro-3-phenyl-1*H*-indene (9): White solid: m.p. 120-121 C; IR (KBr) ν_{max} 3025, 2965, 1634, 1614, 1487, 1477, 1377, 1074, 1025, 755, 695 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 2.9 (apparent m, 2H, *J* = 9Hz, CH_2), 3.3 (s, 2H, CH_2), 3.45 (s, 2H, CH_2), 4.25 (t, 1H, *J* = 9Hz, PhCH) and 7.23 (s, 19H, ArH). MS (EI, 70 eV) m/z (%), 373 (M^+–H, 44.6), 295 (M^+–Ph–2H, 30.3), 281 (M^+–$PhCH_2$–2H, 71.2), 204 (100), 166 (23.7), 115 (3.1), 91 (12.4), 90 (92.1), 77 (5.7), 65 (5.9), 51 (2.3). Anal. Calcd. for $C_{29}H_{26}$ (374): C, 93.04; H, 6.95. Found; C, 92.97; H, 6.83 %.

2-Benzyl-1,2,3,4-tetrahydro-1,4-diphenylnaphthalene (10): White crystals: m.p. 178 °C; R_f 0.46 (silica gel, *n*-hexane/AcOEt; 9.1:0.9); IR (KBr) ν_{max} 3110, 2950, 1634, 1614, 1477, 1447, 1375, 1026, 744, 693 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 2.2 (m, 2H, *J* = 9Hz, cyclic C^3H_2), 2.31 (m, 1, *J* = 9Hz, cyclic C^2H), 2.81 (d, 2H, *J* = 9Hz, $PhCH_2$), 3.89 (d, 1H, *J* = 9Hz, PhC^1H), 4.07 (q, 1H, *J* = 10.5Hz, PhC^4H) and 6.91-7.39 (m, 19H, ArH). MS (EI, 70 eV) m/z (%), 373 (M^+–H, 42.9), 282 (M^+–H–$PhCH_2$, 67.2), 220 (M^+–2Ph, 2.3), 206 (M^+–$PhCH_2$–Ph,

24.2), 166 ($(Ph)_2CH$, 60.2), 129 (M^+–$PhCH_2$–2Ph, 5.7), 91 (100), 65 (7.2), 51 (2.5). Anal Calcd. for $C_{29}H_{26}$ (374): C, 93.04; H, 6.95. Found; C, 92.55; H, 7.12 %.

1,1-Diethyl-2,3-dihydro-3-phenyl-1*H*-indene (13): Yellowish viscous oil; R_f 0.49 (silica gel, *n*-hexane/AcOEt; 9.4:0.6); n_D^{25} 1.6109; IR (Film) ν_{max} 3055, 2975, 1590, 1487, 1445, 1370, 1240, 1070, 1015, 740, 694 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.7 (t, 6H, *J* = 7.5Hz, $2CH_3$), 1.4-1.7 (q, 4H, *J* = 7.5Hz, $2CH_2$), 1.7-2.1 and 2.3-2.5 (m, 2H, *J* = 9Hz, cyclic C^2H_2), 3.9-4.2 (m, 1H, *J* = 9Hz, PhC^3H) and 7.1-7.4 (d, 14H, ArH). MS (EI, 70 eV) m/z (%), 251 (M^++H, 8.1), 250 (M^+, 51.5), 235 (M^+–CH_3, 5.4), 221 (M^+–C_2H_5, 100), 220 (M^+–C_2H_5–CH_3, 69.7), 206 (M^+–C_2H_5–CH_3, 4.8), 192 (M^+–$2C_2H_5$, 20.4), 190 (32.0), 173 (10.1), 166 (12.2), 164 (44.9), 144 (M^+–Ph–C_2H_5, 15.6), 91 (94.3), 77 (15.4), 65 (1.0), 51 (1.7). Anal. Calcd. for $C_{19}H_{22}$ (250): C, 91.2; H, 8.8. Found; C, 90.82; H, 9.05 %.

3-Ethyl-1,1-diphenylpent-2-ene (15): This product was identical in all respects with the prepared authentic sample.

2-Ethyl-1,2,3,4-tetrahydro-1-methyl-4-phenylnaphthalene (14): Faint yellow viscous oil: R_f 0.38 (silica gel, *n*-hexane/AcOEt; 9.4:0.6); n_D^{25} 1.5639; IR (Film) ν_{max} 3070, 3015, 2975, 1595, 1483, 1440, 1370, 1070, 750, 697 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.7 (t, 3H, *J* = 9Hz, CH_3), 1.3 (m, 2H, *J* = 9Hz, CH_2), 1.4 (d, 3H, *J* = 9Hz, CH_3), 1.8 (quin, 1H, *J* = 9 Hz, C^2H), 2.5 (q, 2H, *J* = 9Hz, C^3H_2), 3.4 (quin, 1H, *J* = 9Hz, C^1H), 3.8 (t, 1H, *J* = 9Hz, PhC^4H) and 7.0-7.3 (d, 9H, ArH). MS (EI, 70 eV) m/z (%), 251 (M^++H, 6.5), 248 (M^+–2H, 1.2), 235 (M^+–CH_3, 5.7), 219 (M^+–C_2H_5–2H, 1.0), 205 (M^+–C_2H_5–CH_3–H, 3.7), 190 (32.0), 172 (M^+–Ph-H, 2.0), 166 (100), 164 (33.5), 143 (M^+–Ph–C_2H_5–H, 1.1), 90 (1.1), 77 (2.3). Anal. Calcd. for $C_{19}H_{22}$ (250): C, 91.2; H, 8.8. Found; C, 91.6; H, 8.55 %.

1,1-Diethyl-2,3-dihydro-2-methyl-3-phenyl-1*H*-indene (16): Yellowish viscous oil: n_D^{25} 1.5844; R_f 0.42 (silica gel, *n*-hexane/ benzene, 8.9:1.1); IR (Film) ν_{max} 3060, 3020, 2970, 1595, 1487, 1450, 1375, 1170, 1025, 745, 696 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.6 (t, 6H, *J* = 9Hz, $2CH_3$), 0.9 (d, 3H, *J* = 9Hz, CH_3), 1.5 (q, 4H, *J* = 9Hz, $2CH_2$), 2.2 (m, 1H, *J* = 7.5Hz, cyclic C^2H), 3.9 (d, 1H, *J* = 15Hz, cyclic PhC^3H) and 6.7-7.4 (d, 9, ArH). MS (EI, 70 eV) m/z (%), 264 (M^+, 12.8), 249 (M^+-CH_3, 0.9), 235 (M^+–C_2H_5, 21.8), 210 (M^+–C_2H_5-CH_3, 0.5), 206 (M^+–$2C_2H_5$, 5.7), 191 ((M^+–$2C_2H_5$–CH_3, 3.2), 190 (8.3), 187 (0.2), 166 (100), 164 (23.4), 142 (M^+–Ph–C_2H_5–2H, 3.2), 93 (1.1), 90 (0.5), 77 (0.9). Anal. Calcd. for $C_{20}H_{24}$ (264): C, 90.9; H, 9.09. Found; C, 90.72; H, 9.3 %.

3-Ethyl-2-methyl-1,1-diphenylpent-2-ene (18): This product was identical in all respects with the prepared authentic sample.

2-Ethyl-1,2,3,4-tetrahydro-1,3-dimethyl-4-phenylnaphthalene (17): Yellow viscous oil: n_D^{25} 1.568; R_f 0.36 (silica gel, *n*-hexane/ benzene, 8.9:1.1); IR (Film) ν_{max} 3070, 3010, 2995, 1590, 1485, 1440, 1375, 1075, 1020, 765, 695 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.7 (t, 3H, *J* = 9Hz, CH_3), 0.9 (d, 3H, *J* = 9Hz, C^3HCH_3), 1.3-1.8 (m, 2H, CH_2), 1.5 (d, 2H, *J* = 9Hz, CH_3), 1.9-2.3 (apparent quin, 1H, *J* = 9Hz, C^2H), 2.5-2.7 (q, 1H, *J* =

7.5Hz, C^3H), 3.0-3.4 (apparent q, 1H, *J* = 7.5Hz, C^1H), 3.7 (d, 1H, *J* = 9Hz, PhC^4H) and 6.7-7.3 (d, 9H, ArH). MS (EI, 70 eV) m/z (%), 266 (M^++2H, 2.7), 249 (M^+–CH_3, 1.0), 235 (M^+–C_2H_5, 8.6), 234 (M^+–C_2H_5–H, 20.0), 220 (M^+–C_2H_5–CH_3, 2.5), 206 (M^+–$2C_2H_5$, 4.8), 190 (M^+–$2C_2H_5$–CH_3-H, 10.0), 187 (M^+–Ph, 1.2), 166 (79.8), 164 (100), 142 (M^+–Ph–C_2H_5–2H, 5.0), 93 (1.6), 90 (0.3), 77 (2.5). Anal. Calcd. for $C_{20}H_{24}$ (264): C, 90.9; H, 9.09. Found; C, 92.21; H, 8.75 %.

1,1-Diethyl-2,3-dihydro-2,3-diphenyl-1*H*-indene (19): Yellowish viscous oil: R_f 0.44 (silica gel, *n*-hexane/AcOEt, 8.7:1.3); n_D^{25} 1.6159; IR (Film) ν_{max} 3040, 2985, 1595, 1580, 1480, 1445, 1070, 1025, 750, 700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.8 (t, 6H, *J* = 7.5Hz, $2CH_3$), 2.25 (q, 4H, *J* = 7.5Hz, $2CH_2$), 3.7 (d, 1H, *J* = 9Hz, PhC^2H), 4.5 (d, 1H, *J* = 9Hz, PhC^3H) and 6.6-7.4 (d, 14H, ArH). MS (EI, 70 eV) m/z (%), 326 (M^+, 0.3), 311 (M^+–CH_3, 0.2), 297 (M^+–C_2H_5, 3.6), 268 (M^+–$2C_2H_5$, 1.4), 249 (M^+–Ph, 0.9), 234 (M^+–Ph–CH_3, 0.4), 219 (M^+–Ph–C_2H_5–H, 1.2), 172 (M^+–2Ph, 0.2), 167 (45.0), 166 (100), 164 (56.1), 151 (25.1), 143 (M^+–2Ph–C_2H_5–3H, 0.2), 91 (1.8), 90 (16.2), 77 (8.9). Anal. Calcd. for $C_{25}H_{26}$ (326): C, 92.02; H, 7.97. Found; C, 91.84; H, 7.82 %.

2-Ethyl-1,2,3,4-tetrahydro-1-methyl-3,4-diphenylnaphthalene (20): Faint yellow viscous oil: R_f 0.32 (silica gel, *n*-hexane/AcOEt, 8.7:1.31); n_D^{25} 1.5929; IR (Film) ν_{max} 3050, 2960, 1580, 1480, 1440, 1370, 1080, 768, 695 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.8 (t, 3H, *J* = 7.5Hz, CH_3), 1.2 (d, 3H, *J* = 9Hz, CH_3), 1.3-1.7 (m, 2H, *J* = 7.5Hz, CH_2), 2.1-2.3 (apparent quin, 1H, *J* = 7.5Hz, C^2H), 2.4-2.8 (q, 1H, *J* = 7.5Hz, C^1H), 3.3-3.6 (t, 1H, *J* = 9Hz, PhC^3H), 3.9 (d, 1H, *J* = 9 Hz, PhC^4H) and 6.9-7.4 (d, 14H, ArH). MS (EI, 70 eV) m/z (%), 325 (M^+–H, 0.4), 297 (M^+–C_2H_5, 1.5), 268 (M^+–$2C_2H_5$, 1.2), 256 (4.9), 249 (M^+–Ph, 0.2), 234 (M^+–Ph-CH_3, 0.6), 220 (M^+–Ph–C_2H_5, 0.8),178 (19.2), 171 (M^+–2Ph–H, 0.1), 167 (19.5), 166 (100), 164 (20.4), 151 (10.0), 143 (M^+–2Ph–C_2H_5–3H0, 0.1), 91 (1.1), 90 (8.4), 77 (1.4). Anal. Calcd. for $C_{25}H_{26}$ (326): C, 92.02; H, 7.97. Found; C, 92.3; H, 7.72 %.

1,1,4-Triphenyl-1-butene (21): White crystals: mp 115-17 °C (Lit. mp 122-4 °C [29]); IR (Film) ν_{max} 3060, 2930, 1595, 1490, 1440, 1360, 1065, 750, 693 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 2.4 (t, 2H, *J* = 6Hz, CH_2), 2.6 (t, 2H, *J* = 6Hz, CH_2), 6.0 (t, 1H, *J* = 6Hz, CH) and 7.0-7.4 ppm (m, 15H, ArH). MS (EI, 70 eV) m/z (%), 284 (M^+, 4.7), 283 (M^+-H, 19.5), 207 (M^+-Ph, 2.7), 192 (100), 181 (20.6), 177 (19.7), 166 (5.3), 164 (12.7), 130 (M^+-2Ph, 1.9), 99 (40.4), 91 (0.2), 77 (0.4).

1,1-Diphenyl-1,2,3,4-tetrahydrolnaphthalene (22)[30]**:** Yellow viscous oil: (R_f 0.29, petroleum ether (60-80°C)/AcOEt; 8.9:1.1); n_D^{25} 1.6233; IR (Film) ν_{max} 3050, 3010, 2930, 1595, 1482, 1440, 1060, 770, 696 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 1.5 (quin, 2H, *J* = 6Hz, C^3H_2), 2.55 (t, 2H, *J* = 6Hz, C^2H_2), 2.8 (t, 2H, *J* = 6Hz, C^4H_2) and 6.7-7.8 ppm (m, 14H, ArH). MS (EI, 70 eV) m/z (%), 284 (M^+, 26.7), 283 (M^+-H, 100), 251 (18.2), 207 (M^+-Ph, 11.6), 206 (60.2), 190 (15.0), 166 (5.3), 164 (22.3), 130 (M^+-2Ph, 1.6), 128 (M^+-2Ph-2H, 16.6), 113 (10.4), 91 (0.3), 90 (0.3), 77 (0.2). Anal. Calcd.

for $C_{22}H_{20}$ (284); C, 92.95; H, 7.04. Found; C, 92.62; H, 7.22.

Synthesis of reference samples

3-Ethyl-1,1-diphenylpent-2-ene (15): Dehydration of alcohol **3** by $AcOH/H_2SO_4$ following reported procedure[21] and purification by FC [neutral alumina, petroleum ether (60-80°C) eluent] gave (77.3 %) of pure alkene **20** in the form of yellowish viscous oil: R_f 0.31 (silica gel, *n*-hexane/AcOEt; 9.4:0.6); n_D^{25} 1.5937; IR (Film) ν_{max} 3055, 2975, 1590, 1487, 1445, 1370, 1070, 1025, 750, 694 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 0.7 (t, 6H, *J* = 7.5Hz, $2CH_3$), 1.7 (m, 4H, *J* = 7.5Hz, $2CH_2$), 3.9 (d, 1H, *J* = 6Hz, CH), 5.4 (d, 1H, *J* = 7.5Hz, $(Ph)_2CH$) and 7.0-7.3 (m, 10H, ArH). MS (EI, 70 eV) m/z (%), 251 (M^++H, 1.7), 250 (M^+, 24.6), 235 (M^+–CH_3, 0.2), 221 (M^+–C_2H_5, 35.2), 220 (M^+–C_2H_5–H, 69.7), 206 (M^+– C_2H_5–CH_3, 1.6), 192 (5.6), 173 (1.7), 166 (100), 164 (69.0), 144 (M^+–Ph–C_2H_5, 23.6), 91 (4.2), 90 (39.7), 83 (0.8), 77 (2.9), 65 (2.5). Anal. Calcd. for $C_{19}H_{22}$ (250): C, 91.2; H, 8.8. Found; C, 91.42; H, 8.6 %.

3-Ethyl-2-methyl-1,1-diphenylpent-2-ene (18): Dehydration of 3-ethyl-2-methyl-1,1-diphenyl-3-pentanol (**4**) by $AcOH/H_2SO_4$ and purification by FC [neutral alumina, petroleum ether (60-80°C) eluent] gave (75.5%) of pure alkene **23** in the form of yellowish viscous oil: n_D^{25} 1.5373; R_f 0.30 (silica gel, *n*-hexane/ benzene, 8.9:1.1); IR (Film) ν_{max} 3070, 3030, 2940, 1595, 1480, 1445, 1375, 1085, 770, 695 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$, ppm), δ = 1.3 (d, 6H, *J* = 7.5Hz, $2CH_3$), 1.5 (s, 3H, CH_3), 2.2 (q, 4H, *J* = 7.5Hz, $2CH_2$), 5.9 (s, 1H, $(Ph)_2CH$) and 6.7-7.3 (t, 10H, ArH). MS (EI, 70 eV) m/z (%), 264 (M^+, 1.6), 248 (M^+–CH_3–H, 1.2), 235 (M^+–C_2H_5, 5.7), 222 (5.4), 219 (M^+–C_2H_5–CH_3–H, 1.0), 206 (M^+–$2C_2H_5$, 1.3), 191 (M^+–$2C_2H_5$–CH_2, 6.5), 185 (M^+–Ph–2H, 1.6), 166 (100), 164 (33.5), 143 (M^+–Ph–C_2H_5–H, 1.1), 93 (1.3), 90 (1.1), 77 (1.0). Anal. Calcd. for $C_{25}H_{26}$ (326): C, 90.9; H, 9.09. Found; C, 91.2; H, 8.72 %.

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