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On the π–π Interaction in the Benzylation of Ketones

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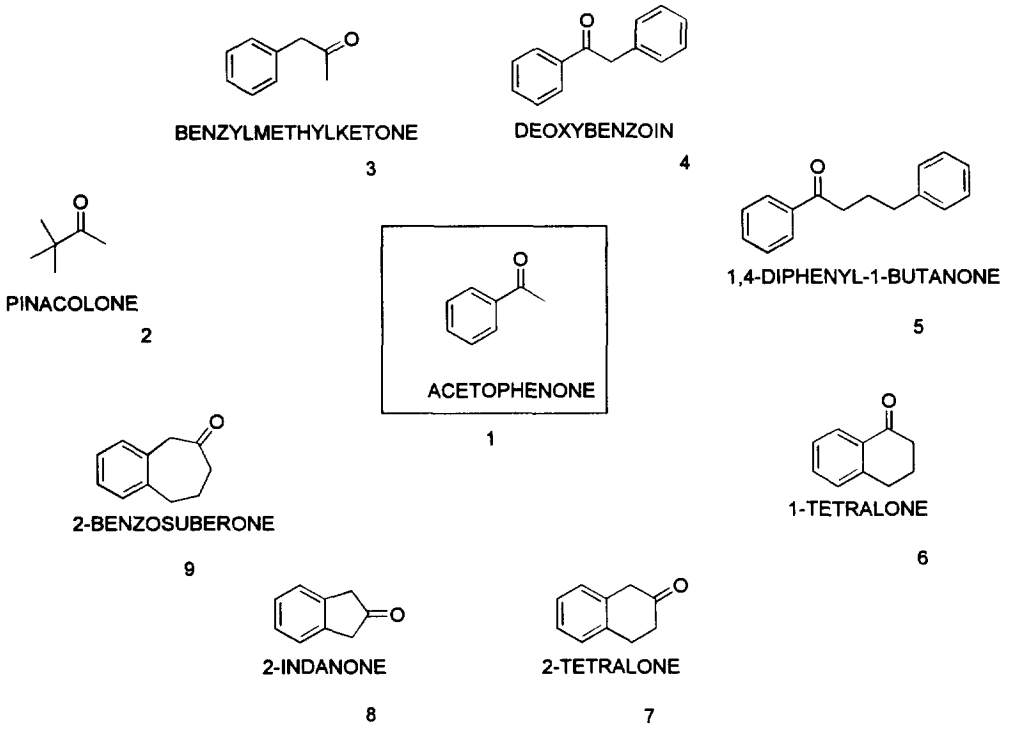
Abstract. The benzylation of a set of nine ketones provides enough information to establish how the ketone structure affects the existence of a π–π interaction. The presence of a phenyl moiety starting from the α-carbon atom and flexibility in cyclic ketones are structural features required for effective interactions. The π–π interaction is controlled by a polar-π effect. Stronger interaction is achieved when slight electronwithdrawing groups are present in both π-system. This results is explained by the predominance of the σ–π shells attractive interaction in an edge-to-face geometry.

π–π Interactions are an important factor in the control of various phenomena such as molecular recognition and asymmetric synthesis.[1] Geometry (mainly the offset between the interacting π–systems and the dihedral angle between the phenyl moieties) is an important factor in assisting or impeding the π–interaction.[2] Theoretical approaches[3] regarding the nature of the π–π interaction reported the existence of two main effects: charge transfer and polar/π (coulombic) effects. A π–π interaction controlled by charge transfer effect becomes stronger when one of the π-systems has electronwithdrawing substituents and the other π-system has electrondonor substituents, whereas when the coulombic effect predominates stronger interaction is achieved when both π-systems contain electronwithdrawing groups. Experimental results in which one or other of the effects predominate have been reported. Thus, for example, the complexation constant for the inclusion of naphtalenic derivatives bearing electronwithdrawing groups into cyclophanes containing alkoxy groups is higher than for the inclusion of electrondonor substituted naphtalenes[4] (predominance of the charge transfer effect), while the energy for the conformational change in 1,8-diarylnaphtalenes increases when both aryl systems have electrowithdrawing substituents[5] (predominance of the coulombic effect).

Recently we reported[6] the undeniable contribution of a π–π interaction in stabilising the transition state of the benzylation of 1,3-diphenyl-1–propanone. In this transition state three different π–π interactions are possible. It is, however the interaction between the benzyl moiety of the substrate and the benzyl moiety of the

electrophile which actually determines the stabilisation. It is this π–π interaction which explain the predominance of the double benzylation product of acetophenone.

In order to establish the influence of the enolate geometry on this π–π interaction we initiated a study on the benzylation of a set of ketones possessing different structural patterns and also we have now considered a set of reactions, in which the substitution patterns on the π-system, have been varied in order to discern whether, the charge transfer or coulombic, effect predominates.

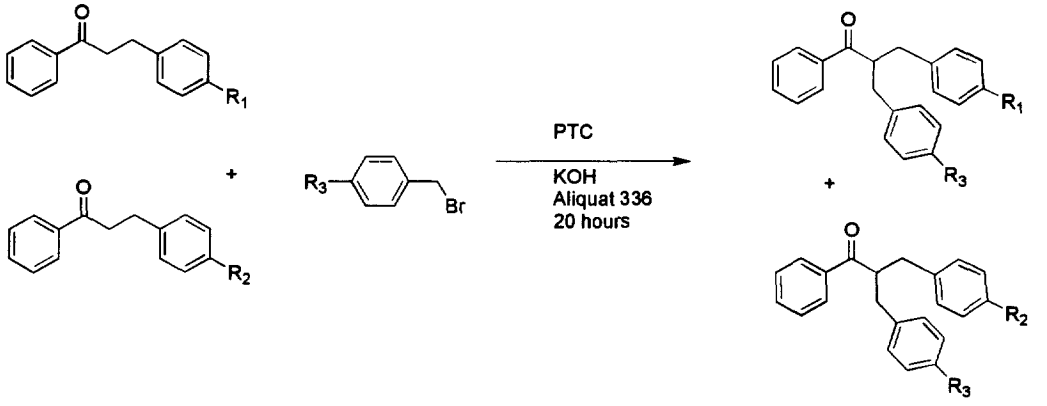


Chart

For the first purpose we choose the ketones showed in the chart. Each one incorporates at least one element which make it different from the parent compound, acetophenone **1**. Thus, in pinacolone **2** no π–systems are present while benzylmethylketone **3** presents a phenyl group in the α position. Deoxybenzoin **4** which has two benzene rings is a substrate which combines the arrangements found in **1** and **3** and 1,4-diphenyl-1-butanone **5** has one carbon atom more than 1,3-diphenyl-1-propanone, the monobenzylation product of acetophenone. 1-Tetralone **6** and 2-tetralone **7**, the cyclic equivalents of **1** and **3** respectively, have been

incorporated in this study in order to verify how the mobility constraint affects the results. 2-Indanone **8** and 2-benzosuberone **9** have been included so as to evaluate the influence of ring constraint.

For the second purpose we performed competitive reactions using equimolar amounts of two differently substituted 1,3-diphenyl-1-propanones with benzyl bromides, according to scheme 1.



Scheme 1

Results and Discussion

Structural Requirements for an Effective Interaction. Benzylation reactions were performed by stirring a mixture of the ketone (**1-9**) (1 mmol), benzyl bromide (2 mmol), finely ground potassium hydroxide (1 mmol) and Aliquat 336[7] (0.1 mmol) as catalyst, at room temperature in the absence of solvent. The reactions were stopped after 3 hours and the crude reactions were analysed by GC and/or ^{1}H-NMR. The results are summarised in the table 1.

Reactions with allyl and propargyl bromides afforded similar results to benzyl bromide. As previously reported[6] reactions with acetophenone and pinacolone afford a slight excess of disubstituted compounds (using larger reaction times dibenzylated compounds were exclusively obtained) and this behaviour can be explained by considering a stabilising π–π interaction. However the rest of the acyclic ketones afforded a predominance of the monoalkylated derivative. This can be rationalised by assuming that the presence of a benzyl moiety, as in the case of the deoxybenzoin creates the possibility of a π–π interaction in the first benzylation, thus favouring monobenzylation with further benzylation occurring, if at all, to only a minor extent. Scheme 2 shows, in a simplified way, these enolates which can establish a π–π interaction to selectively afford monoalkylation products.

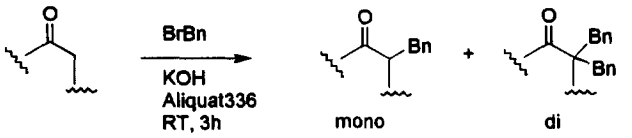
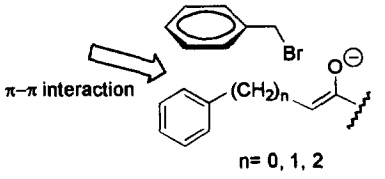


Table 1

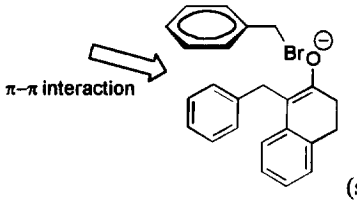
ketone	recovered ketone (%)	mono/di ratio
1	30	45/55
2	<1	40/60
3	<3	91/9
4	19	100/0
5	<2	100/0
6	50	50/50
7	<5	0/100
8	<1	0/100[a)]
9	24	47/53

a) the compound obtained is 1,1-dibenzyl-2-indanone



Scheme 2

1-Tetralone **6**, the cyclic equivalent of acetophenone, behaves similarly to acetophenone. Both ketones can form enolates to give the geometric arrangements which favour the second benzylation (it has been shown that the phenyl group directly bonded to the carbonyl group does not play a determining role in the stabilisation of the transition state).[6] Unlike 1-tetralone, 2-tetralone **7**, behaves quite differently to its acyclic equivalent benzylmethylketone. The dibenzylation product is exclusively obtained with 2-tetralone whereas benzylmethylketone selectively affords the monobenzylated product. This result indicates that the constrained mobility in 2-tetralone prevents the π–π interaction involving the benzene ring of 2-tetralone from taking place. The exclusive formation of the dibenzylation product should be explained by considering the same interaction shown for acetophenone (scheme 3).

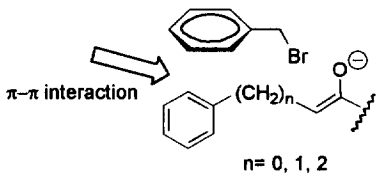


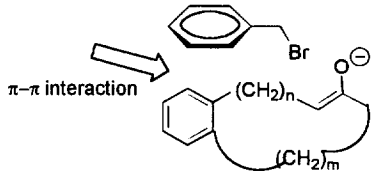
(scheme 2, n = 1)

Scheme 3

The result obtained using 2-indanone **8** can be similarly explained. In this case two dibenzylated compounds may result (1,1-dibenzyl-2-indanone and 1,3-dibenzyl-2-indanone) but only 1,1-dibenzyl-2-indanone was obtained. This product come from the thermodynamic enolate, the only one were the π–π interaction is possible.

The 2-benzosuberone **9** afforded mixtures of mono- and dibenzylated compounds showing that a more flexible ring permits the desired disposition to be established so as to allow a π–π interaction in the first benzylation. It also allows the more complete and generalised structural requirements for the existence of a π–π interaction in the benzylation of ketones (scheme 4) to be established.





n = 0, m>2 and n >0, m >1

Scheme 4

In our previous work we affirmed that the existence of a π–π interaction was a more important factor than the acidity of the ketone. Taking into account the results obtained in this work it is possible to affirm that the structure of the ketone plays a determinant role whereas the acidity is a complementary factor. Hence, two ketones of similar acidities, 2-indanone pKa=16.95 and deoxybenzoin pKa=17.65,[8] show completely different behaviour.

ketone	pKa	mono/di ratio
4	17.65	100/0
8	16.95	0/100

Charge Transfer or Polar/π Predominance. Competitive reactions were performed using the conditions employed for the benzylation of acetophenone (solvent-free PTC, KOH, Aliquat 336, reaction time 20 h).[6] ^{1}H-NMR and/or GC were used to determine the degree of conversion of each ketone.

Table 2 summarises the results obtained using methoxy and trifluoromethyl substituted derivatives on the three phenyl systems involved in the π–π interaction. The column ratio R_1/R_2 represents the conversion of each ketone.

Table 2.

Entry	R_1/R_2	R_3	ratio R_1/R_2
1	H / OCH_3	H	59 / 41
2	H / CF_3	H	33 / 67
3	OCH_3 / CF_3	H	30 / 70
4	H / OCH_3	OCH_3	58 / 42
5	H / CF_3	OCH_3	31 / 69
6	OCH_3 / CF_3	OCH_3	27 / 73
7	H / OCH_3	CF_3	69 / 31
8	H / CF_3	CF_3	17 / 83
9	OCH_3 / CF_3	CF_3	40 / 60

In all cases a higher conversion of the ketone with the lower π-electron density is observed. This result seems to indicate a predominance of the coulombic effect, although the result in entry 5 could be explained considering both effects. Entry 9 is more informative as the charge transfer effect and coulombic effect are tested at the same time and the predominance of the latter is evident.

A new set of reaction was performed increasing the difference in electronic density between the interacting π-systems was increased. The 3,5-dimethoxy and the 3,5-bistrifluoromethyl derivatives were used. The results are collected in Table 3. The polar-π effect contribution largely predominates as revealed by the higher conversion of those ketones having electronwithdrawing groups.

Table 3.

Entry	R_1/R_2	R_3	ratio R_1/R_2
1	3,5-$(OCH_3)_2$ / 3,5-$(CF_3)_2$	H	6 / 94
2	3,5-$(OCH_3)_2$ / 3,5-$(CF_3)_2$	3,5-$(OCH_3)_2$	8 / 92
3	3,5-$(OCH_3)_2$ / 3,5-$(CF_3)_2$	3,5-$(CF_3)_2$	7 / 93

In order to verify if the predominance of the coulombic effect is a general behaviour we incorporated into this study the nitro and the cyano groups (electronwithdrawing groups by conjugative effect). Accordingly a set of reactions (Table 4) were performed using the reaction conditions expressed before.

Table 4.

Entry	R_1/R_2	R_3	ratio R_1/R_2
1	OCH_3 / NO_2	H	43 / 57
2	OCH_3 / CN	H	32 / 68
3	H / CN	H	36 / 64
4	CF_3 / CN	H	60 / 40
5	CF_3 / NO_2	H	60 / 40
6	CN / NO_2	H	52 / 48
7	OCH_3 / NO_2	CF_3	47 / 53
8	CF_3 / CN	CF_3	55 / 45
9	OCH_3 / CN	CN	28 / 72
10	OCH_3 / NO_2	CN	41 / 59
11	CF_3 / CN	CN	55 / 45
12	OCH_3 / NO_2	NO_2	47 / 53
13	CF_3 / CN	NO_2	53 / 47

Two main observations can be derived from these results: i) whatever the nature of the substituent, ketones bearing electronwithdrawing groups are more reactive (entries 1, 2, 3, 7, 9, 10 and 12), and ii) the ketone reactivity increase as the electrowithdrawing power is reduced; thus $CF_3 > CN > NO_2$ (see entries 6 and 8, and compare entries 1 and 2, entries 4 and 5, entries 9 and 10 or entries 11 and 13).

It can be affirmed that the polar-π (coulombic) effect predominates in the interaction proposed but the order observed ($CF_3 > CN > NO_2$) needs an explanation. This result indicates that the interaction between two π-systems bearing, for example., trifluoromethyl in both systems is stronger than the interaction between two systems bearing a trifluoromethyl and a cyano group. Previous work on 1,8-diarylnaphtalenes,[5] where a predominance of a polar-π effect was shown, indicated that the interaction is stronger when the π-electron density is lower; this is a result of a lower repulsion between the π-shells in a face-to-face geometry. As suggested,[9] in an edge-to-face geometry attractive interactions between σ–π shells are possible and the final situation is a result of both, π–π and σ–π, interactions. The σ–π interactions are stronger when both, σ- and π-density are higher; thus a σ–π interaction between two π-systems bearing two trifluoromethyl groups is stronger than the interaction between two systems bearing a trifluoromethyl and a cyano group [σ (CF_3) <> π

(CF_3) > σ (CF_3) <> π (CN)]. This results is in agreement with the geometry calculated for the transition state (dihedral angle: 71°, offset: 5.6 Å).[6]

Several conclusions can be drawn: i) the mono/di selectivity in the alkylation of ketones using alkyl halides bearing a π–system can be predicted by considering the ketone structure, thus ketones bearing a phenyl group starting from the α-carbon atom and ketones non constricted by the existence of a condensed ring yield selectively monoalkylation products; ii) the π–π interaction studied in this work is controlled by the polar-π or coulombic effect, and iii) in an edge-to-face geometry the interaction between σ- and π-shells compensates the repulsion between the π-shells; thus a more effective π–π interaction can be achieved using slight electronwithdrawing groups.

Experimental Section

^{1}H-NMR spectra were recorded at 300 MHz (Varian Unity 300) in $CDCl_3$; chemical shifts are reported in δ units (ppm) relative to tetramethylsilane and coupling constants expressed in Hz. GC analyses were performed on Konik 3000 and Carlo Erba GC 6000 apparatuses using hydrogen and helium respectively as the carrier. Elemental analyses were performed on a Perkin Elmer PE2400 CHN elemental analyser.

All solvents used for extractions or reactions in solid-liquid or liquid-liquid PTC were dried according to standard procedures and kept over molecular sieves. 3-Aryl-1-phenyl-1-propanones were synthesised from the corresponding chalcones[10] by hydrogenation following the Hantzsch method[11] for nitro substituted chalcone, and the ammonium formate method[12] for the rest and have been previously reported,[6] except:

1-Phenyl-3-[3', 5'-bis(methoxy)phenyl]-1-propanone: mp 58.0-59.0°C (ethanol/water). ^{1}H-NMR: 2.90 t (2H, CH_2Ph, J=7.5), 3.17 (t, 2H, $COCH_2$, J=7.5), 3.65 [s, 6H, 2 x (OCH_3)], 6.20-7.85 (m, 8H, arom.). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%. Found: C, 75.77; H, 6.65%.

1-Phenyl-3-[3', 5'-bis(trifluoromethyl)phenyl]-1-propanone: mp 48.8-50.0°C (ethanol/water). ^{1}H-NMR: 3.22 (t, 2H, CH_2Ph, J=7.0), 3.37 (t, 2H, $COCH_2$, J=7.0), 7.20-8.00 (m, 8H, arom.). Anal. Calcd for $C_{17}H_{12}F_6O$: C, 58.92; H, 3.49%. Found: C, 58.77; H, 3.65%.

1-Phenyl-3-(p-cyanophenyl)-1-propanone: mp 91.5-92.4°C (ethanol/water). ^{1}H-NMR: 3.30 (t, 2H, CH_2Ph, J=7.0), 3.70 (t, 2H, $COCH_2$, J=7.0), 7.40-8.00 (m, 9H, arom.). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95%. Found: C, 81.99; H, 5.65; N, 6.12%.

1-Phenyl-3-(p-nitrophenyl)-1-propanone: mp 98.2-98.4°C (ethanol/water). ^{1}H-NMR: 3.40 (t, 2H, CH_2Ph, J=7.1), 3.70 (t, 2H, $COCH_2$, J=7.1), 7.60-8.30 (m, (9H, arom.). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%. Found: C, 70.79; H, 5.35; N, 5.42%.

2-Benzosuberone was prepared by literature methods,[13] and the rest of chemicals are commercially available.

General procedure for alkylations. Ketone (10 mmol), finely ground potassium hydroxide (10 mmol) and Aliquat 336 (1 mmol) were stirred at room temperature for 5 min. Then, the appropriate alkyl halide (10 mmol) was added and the reaction was stirred for the appropriate time. The crude reaction mixture was extracted with dichloromethane (2 x 25mL) and analysed by GC or ^{1}H-NMR.

1,3-Diphenyl-1-propanone, 2-benzyl-1,3-diphenyl-1-propanone, 1-phenyl-3-(p-methoxyphenyl)-1-propanone, 1-phenyl-3-(p-trifluoromethylphenyl)-1-propanone, 1-phenyl-4-penten-1-one, 1-phenyl-2-allyl-4-penten-1-one, 1-phenyl-4-pentyn-1-one and **1-phenyl-2-propargyl-4-pentyn-1-one** have been previously reported.[6] The rest of alkylation products have been not isolated. The analyses have been directly performed on the ^{1}H-NMR spectra of the reaction crudes. Chemical shifts and coupling constants are summarised below.

1-Phenyl-4,4-dimethyl-3-pentanone: 1.09 [s, 9H, 3 x (CH_3)], 2.78 (t, 2H, *CH_2*Ph, J=6.6), 2.85 (t, 2H, $COCH_2$, J=6.6), 7.00-7.40 (m, 5H, arom.).

2-Benzyl-1-phenyl-4,4-dimethyl-3-pentanone: 0.75 [s, 9H, 3 x (CH_3)], 2.58-2.93 [2 x dd, 4H, 2 x (CH_2Ph), J=13.2, J=7.8, J=6.6], 3.45 (tt, 1H, CH, J=7.8, J=6.6), 7.00-7.40 (m, 10H, arom.).

2,2-Dimethyl-6-hepten-3-one: 1.14 [s, 9H, 3 x (CH_3)], 2.25-2.35 (m, 2H, *CH_2*$CHCH_2$), 2.58 (t, 2H, $COCH_2$, J=7.4), 4.90-5.10 (m, 2H, CH*CH_2*), 5.60-5.90 (m, 1H, *CH*CH_2).

4-Allyl-2,2-dimethyl-6-hepten-3-one: 1.13 [s, 9H, 3 x (CH_3)], 2.09-2.40 [2 x ddd, 4H, 2 x (*CH_2*$CHCH_2$), J=13.4, J=6.8, J= 6.8], 3.05 (q, 1H, CH, J=6.8), 4.90-5.10 [m, 4H, 2 x (CH*CH_2*)], 5.60-5.90 [m, 2H, 2 x (*CH*CH_2)].

2,2-Dimethyl-6-heptyn-3-one: 1.19 [s, 9H, 3 x (CH_3)], 1.93 [t, 2H, 2 x (CCH), J=2.7], 2.40-2.60 (m, 2H, *CH_2*CCH), 2.75 (t, 2H, $COCH_2$, J=7.4).

2,2-Dimethyl-4-propargyl-6-heptyn-3-one: 1.20 [s, 9H, 3 x (CH_3)], 2.02 [t, 2H, 2 x (C*CH*), J=2.7], 2.49-2.99 [2 x ddd, 4H, 2 x (*CH_2*CCH), J=16.9, J=7.1, J=2.7], 3.38 (q, 1H, CH, J=7.1).

3,4-Diphenyl-2-butanone: 2.05 (s, 3H, CH_3), 2.90-2.97 (dd, 1H, C*H*HPh, J=13.8, J=7.4), 3.43-3.50 (dd, 1H, CH*H*Ph, J=13.8, J=7.4), 3.96 (t, 1H, *CH*CH_2, J=7.4), 7.00-7.40 (m, 10H, arom.).

3-Benzyl-3,4-diphenyl-2-butanone: 2.09 (s, 3H, CH_3), 3.37 [s, 4H, 2 x (CH_2Ph)], 7.00-7.40 (m, 15H, arom.).

3-Phenyl-5-hexen-2-one: 2.04 (s, 3H, CH_3), 2.38-2.44 (ddd, 1H, C*H*H$CHCH_2$, J=14.3, J=7.4, J=7.1), 2.74-2.81 (ddd, 1H, CH*H*$CHCH_2$, J=14.3, J=7.4, J=7.1), 3.68 (t, 1H, *CH*CH_2, J=7.4), 4.85-5.00 (m, 2H, CH*CH_2*), 5.50-5.70 (m, 1H, *CH*CH_2), 7.10-7.20 (m, 5H, arom.).

3-Allyl-3-phenyl-5-hexen-2-one: 2.05 (s, 3H,CH_3), 2.74-2.81 [m, 4H, 2 x (*CH_2*$CHCH_2$)], 4.85-5.00 [m, 4H, 2 x (CH*CH_2*)], 5.50-5.70 [m, 2H, 2 x (*CH*CH_2)], 7.10-7.40 (m, 5H, arom.).

3-Phenyl-5-hexyn-2-one: 1.85 (t, 1H, CCH, J=2.4), 2.02 (s, 3H, CH_3), 2.24-3.10 (ddd, 2H, *CH_2*CCH, J=16.8, J=7.0, J=2.4), 3.85 (t, 1H, *CH*CH_2, J=7.0), 7.10- 7.40 (m, 5H, arom.).

3-Phenyl-3-propargyl-5-hexyn-2-one: 1.90 (t, 1H, C*CH*, J=2.8), 1.95 (s, 3H, CH_3), 3.02 [d, 4H, 2 x (*CH_2*CCH), J=2.8], 7.05-7.65 (m, 5H, arom.).

1,2,3-Triphenyl-1-propanone: 3.03-3.10 (dd, 1H, C*H*HPh, J=13.7, J=7.4), 3.53-3.60 (dd, 1H, CH*H*Ph, J=13.7, J=7.4), 4.81 (t, 1H, *CH*CH_2, J=7.4), 7.00-8.00 (m, 15H, arom.).

1,2-Diphenyl-4-penten-1-one: 2.52-2.62 (ddd, 1H, C*H*HCHCH_2, J=14.2, J=7.4, J=7.1), 2.91-3.00 (ddd, 1H, CH*H*CHCH_2, J=14.2, J=7.4, J=7.1), 4.63 (t, 1H, *CH*CH_2, J=7.4), 4.94-5.08 (m, 2H, CH*CH_2*), 5.68-5.81 (m, 1H, *CH*CH_2), 7.20-8.00 (m, 10H, arom.).

1,2-Diphenyl-4-pentyn-1-one: 1.93 (t, 1H, CCH, J=2.7), 2.65-2.74 (ddd, 1H, C*H*HCCH, J=16.8, J=7.3, J=2.7), 2.99-3.08 (ddd, 1H, CH*H*CCH, J=16.8, J=7.3, J=2.7), 4.78 (t, 1H, $CHCH_2$, J=7.3), 7.10-8.00 (m, 10H, arom.).

2-Benzyl-1,4-diphenyl-1-butanone: 2.00-2.70 (m, 4H, CH_2CH_2), 2.75-3.20 (2 x dd, 2H, CH*CH_2*Ph, J=15.2, J=5.0), 3.71 (q, 1H, CH, J=5.0), 7.00-8.00 (m, 15H, arom.).

2-Benzyl- 3,4-dihydro-1(2H)naphtalenone: 2.08-2.14 (m, 1H, CH), 2.60-2.80 (m, 2H, CH_2-3), 2.60-3.53 (m, 2H, *CH_2*Ph), 2.94 (t, 2H, CH_2-4, J=5.0), 7.20-8.10 (m, 9H, arom.).

2,2-Dibenzyl- 3,4-dihydro-1(2H)naphtalenone: 1.92 (t, 2H, CH_2-3, J=6.0), 2.65 (d, 2H, CH_2, J=13.2), 3.02 (t, 2H, CH_2-4, J=6.0), 3.30 (d, 2H, CH_2, J=13.2), 7.00-8.10 (m, 14H, arom.).

2-Allyl- 3,4-dihydro-1(2H)naphtalenone: 1.80-1.92 (m, 1H, CH), 2.19-2.80 (m, 4H, *CH_2*CH=CH2; CH_2-3), 2.75 (t, 2H, CH_2-4, J=5.0), 5.00-5.10 (m, 2H, CH*CH_2*), 5.75-5.90 (m, 1H, *CH*CH_2), 7.20-8.10 (m, 4H, arom.).

2,2-Diallyl-3,4-dihydro-1(2H)naphtalenone: 2.03 (t, 2H, CH_2-3, J=6.5), 2.24-2.31 (dd, 2H, CH_2, J=13.9, J=7.6), 2.47-2.54 (dd, 2H, CH_2, J=13.9, J=7.6), 2.99 (t, 2H, CH_2-4, J=6.5), 5.00-5.10 [m 4H, 2 x (CH*CH_2*)], 5.70-5.82 [m, 2H, 2 x (*CH*CH_2)], 7.20-8.10 (m, 4H, arom.).

3,4-Dihydro-2-propargyl-1(2H)naphtalenone: 2.00 (t, 1H, C*CH*, J=2.7), 2.40-2.60 (m, 3H, CH; CH_2-3), 2.87-2.96 (ddd, 2H, *CH_2*CCH, J=16.9, J=4.2, J=2.7), 3.18 (t, 2H, CH_2-4, J=4.2), 7.20-8.10 (m, 4H, arom.).

3,4-Dihydro-2, 2-dipropargyl-1(2H)naphtalenone: 2.04 [t, 2H, 2 x (CCH), J=2.7], 2.39 (t, 2H, CH_2-3, J=6.4), 2.53-2.74 [2 x dd, 4H, 2 x (CH_2), J=16.9, J=2.7], 3.04 (t, 2H, CH_2-4, J=6.4) , 7.24-8.05 (m, 4H, arom.).

1,1-Dibenzyl- 3,4-dihydro-2(1H)naphtalenone: 2.04 [t, 2H, 2 x (CCH), J=2.7], 2.39 (t, 2H,CH_2-3, J=6.4), 2.53-2.74 [2 x dd, 4H, 2 x (CH_2), J=16.9, J=2.7], 3.04 (t, 2H, CH_2-4, J=6.4), 7.24-8.05 (m, 14H, arom.).

1,1-Diallyl- 3,4-dihydro-2(1H)naphtalenone: 2.50 (t, 2H, CH_2-3, J=7.0), 2.50-2.78 [2 x dd, 4H, 2 x (CH_2), J=13.4, J=8.3], 2.95 (t, 2H, CH_2-4, J=7.0), 4.85-5.00 [m, 4H, 2 x (CH*CH_2*)], 5.30-5.45 [m, 2H, 2 x (*CH*CH_2)], 7.20-8.00 (m, 4H, arom.).

3,4-Dihydro-1,1-dipropargyl-2(1H)naphtalenone: 1.86 [t, 2H, 2 x (CCH), J=2.7], 2.68-2.89 [2 x dd, 4H, 2 x (CH_2), J=16.6, J=2.7], 2.70 (t, 2H, CH_2-3, J=7.0), 3.14 (t, 2H, CH_2-4, J=7.0), 7.10-7.40 (m, 4H, arom.).

1,1-Dibenzyl-1,3-dihydro-2H-indan-2-one: 2.63 (s, 2H, CH_2), 3.06-3.36 [2 x d, 4H, 2 x (CH_2Ph), J=13.0], 6.75-7.50 (m, 14H, arom.).

5-Benzyl-5,7,8,9-tetrahydro-6H-benzocyclohepten-6-one: 1.70-2.75 (m, 6H, CH_2 cicl.), 2.90-3.70 (dd, 2H, CH_2Ph, J=12.6, J=7.6), 4.12 (t, 1H, CH, J=7.6), 6.75-7.40 (m, 9H, arom.).

5-Dibenzyl-5,7,8,9-tetrahydro-6H-benzocyclohepten-6-one: 1.70-2.75 (m, 6H, CH_2 cycl.), 3.25 (s, 4H, 2 x (CH_2Ph), 6.75-7.40 (m, 14H, arom.).

1-Phenyl-2-(p-methoxybenzyl)-3-(p-trifluoromethylphenyl)-1-propanone: 2.69-3.22 [4 x dd, 4H, 2 x (CH_2), J=13.5, J=7.0, J=5.5], 3.75 (s, 3H, OCH_3), 3.93-4.01 (tt, 1H, CH, J=7.0, J=5.5), 6.75-7.70 (m, 13H, arom.).

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