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AROMATIZATION OF ALIPHATIC COMPOUNDS—V[1]

m-DIALKYL-BENZENES AND 2-BENZYL-NAPHTHALENES

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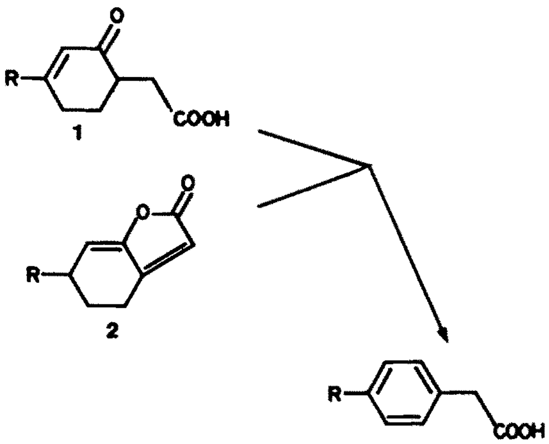
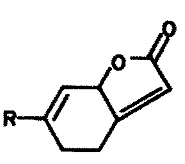
Abstract—Some cyclohexadienols, when heated at 220° with PyHCl, gave, through dehydration and isomerisation, the corresponding benzene derivatives. So 2,6-dibenzyliden-cyclohexanols gave *m*-dibenzyl-benzenes, 2-benzyliden-1-tetralols gave 2-benzyl-naphthalenes and 2,6-dicyclohexenyl cyclohexanols gave *m*-dicyclohexyl-benzenes. The correlation between these aromatisations and those of cyclohexenone acetic acids to arylacetic acids are here discussed. Some by-products, which were obtained in the aromatisation of 2-benzylidene-1-tetralols, are also described.

Some cyclohexenone acetic acids **1** and some dihydrobenzofuranones **2**, when treated with pyridine hydrochloride (PyHCl), undergo aromatisation to arylacetic acids **3**.[1,2]



The diallylic alcohol derivatives **4** and **5**, which were proposed as intermediates in the aromatisation of cyclohexenone acetic acids **1**,[2] may also be thought to be the intermediates in the dihydrobenzofuranones **2** aromatisation.



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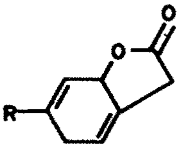

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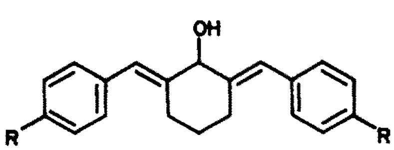
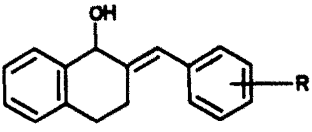
In order to test the plausibility of this hypothesis we investigated the behaviour towards PyHCl, of some 2,6 dibenzylidene-cyclohexanols **6**:



6 (a, b, c, d)

a: R = H
b: R = Cl
c: R = NO_2
d: R = CH_3

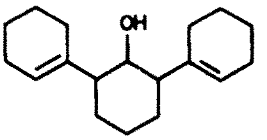
and of some 2-benzylidene-1-tetralols **7**



7 (a, b, c, d, e, f)

a: R = H
b: R = p-Cl
c: R = P-NO_2
d: R = p-CH_3
e: R = p-CN
f: R = o-CH_3

In order to complete our investigation we also included the study of the two non-allylic isomeric dienols **8** and **9**



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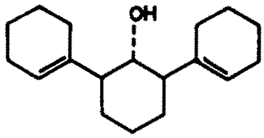

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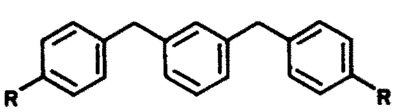
The dibenzylidene-cyclohexanols (two of which already described in literature) were obtained, according to the known procedure,[3] by a $NaBH_4$ reduction of the corresponding dibenzylidene-cyclohexanones.

By heating these compounds for a short time at 200–220° with PyHCl, the corresponding *m*-dibenzylbenzenes **10** were obtained, thus compounds **6a**,[3] **6b**[3] **6c** and **6d** gave the corresponding compounds (yield %): **10a**[4] (45), **10b** (44), tars, **10d** (38).



10 (a, b, d)

The aromatic products **10** were purified by distillation followed by recrystallisation and no effort was made for the detection of possible by-products.

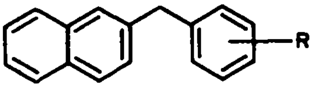
The behaviour of 2-benzylidene-1-tetralols **7** towards PyHCl proved to be more complex. All the compounds **7** reported in the table many of which are already described in literature, were obtained by $NaBH_4$ reduction of the corresponding ketones.

It was again possible, by heating at 200–220° with PyHCl for a short time, to obtain from the compounds **7a, b, d, e** the corresponding 2-benzylnaphthalenes **11**

Table 1. Aromatisation of 2-benzylidene-1-tetralols

TETRALOL	R	REACTION TIME AND TEMPERATURE	PRODUCT	YIELD %
7a[5]	H	15', 220°C	11a[6]	30*
7b[7]	p-Cl	20', 220°C	11b[8]	51
7c[7]	p-NO_2	10', 210°C	tars	
7d[7]	p-CH_3	20', 215°C	11d[8]	33
7e	p-CN	10', 215°C	11e	57
7f	o-CH_3	20', 215°C	12	25

* Isolated as picrate



11 (a, b, d, e)

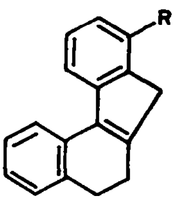
in preparative yields by purification of the crude reaction mixtures through simple recrystallisation or via picrates (Table 1).

Nevertheless, except for 7e, several by-products were always found together with the 2-benzyl-naphthalenes. In particular we studied, in glc/Mass, the crude mixture obtained from 7a. Five peaks were detected: a major peak (B) due to 2-benzyl-naphthalene, a peak with a shorter r.t. (A) due to a dihydrobenzyl-naphthalene, a peak with a longer r.t. (C) isomeric to 2-benzyl-naphthalene but different from the 1-benzyl isomer[9] and, at last, two partially superimposed peaks (D, E) identified as *E* and *Z* isomers of 2-benzylidene-1-tetralone.

As regards the substance corresponding to peak C it shows in the glc/MS analysis a molecular peak with a mass corresponding to $C_{17}H_{14}$. A peak with the same r.t. and the same mass spectrum was also obtained, in small quantities from the pyrolysis of 2-benzyl-naphthalene in contrast with Graebe[10] which assigned the formula $C_{17}H_{12}$ to the pyrolysis product of 2-benzyl-naphthalene.[11]

The glc analysis of the crude mixture showed the same pattern already described for the crude mixture obtained from all the other 2-benzylidene-1-tetralols (except for 7e) submitted to PyHCl treatment. The only difference remarked is the relative heights of the peaks. In the case of 7f (R = *o*-Me), the major peak noticed in the glc analysis was the one corresponding to peak C. From recrystallisation of the crude mixture we did not obtain the 2-(*o*-methylbenzyl)-naphthalene but the substance relative to peak C.

This compound, from the elemental analysis and NMR spectrum, showed to be the 7H-8-methyl-5,6-dihydro-benzo/c/fluorene 12.



12: R = CH_3
13: R = H

Based on the analogy of the above results the structure of 7H - 5,6 - dihydro - benzo/c/fluorene 13 was assigned to the substance relative to peak C of the crude mixture obtained from 7a.

The dienols 8 and 9 were obtained in mixture by $NaBH_4$ reduction of the known 2,6 - dicyclohexenyl - cyclohexanone.[12] After column chromatographic separation, the drafted structures were assigned to each substance on the basis of their NMR spectra.[13]

Differing from the described diallylic alcohols, much more time is necessary to obtain the disappearance of the starting products both for 8 and for 9, when treated with PyHCl.

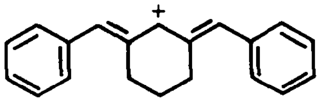
From the crude mixture obtained from 9, *m*-dicyclohexyl-benzene was separated by distillation, which showed a single peak in glc; on the contrary a mixture, showing in glc the presence of *m*-dicyclohexylbenzene in addition to other peaks, was obtained from 8.

The reactions above described were not obvious since the 2-benzyl-naphthalene itself was recently obtained, starting from the alcohol 7a, in two steps i.e. hydrogenolysis followed by dehydrogenation with Pd(C).[14]

From a mechanistic point of view the diallylic cycloalkanols, when treated with PyHCl, undergo an easy aromatisation via cations 14 and 15 through a double bound isomerisation, allylic transposition and final loss of a proton. In the more investigated case of tetralols we also noticed a disproportionation which leads to the dihydro derivative and to the corresponding benzylidene-tetralones.

This fact is not surprising when we consider that these substances are vinylogous of benzydrol, a substance in which an acid-catalysed disproportionation has been found and described.[15]

It also seems reasonable the formation of the dihydrobenzo/c/fluorenes by intramolecular alkylation of the cation 15.



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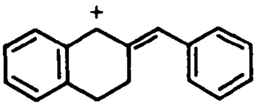

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Both these side reactions are obviously favoured by the activating substituents of the benzene nucleus and disfavoured by the disactivating ones,[15] taking therefore into account the extreme behaviours of di-*p*-methoxy-benzylidene-cyclohexanols and *p* - cyano - benzylidene - tetralol respectively.

As to the greater difficulty for the aromatisation of the two isomeric dicyclohexenyl - cyclohexanols, this seems due to a greater difficulty in forming an initial carbonium ion which is less stabilised than an allylic one. More particularly the behaviour of **8** may be attributed to the facility of this compound to undergo a transelimination of water with formation of a trienic compound for which the isomerisation to *m*-dicylohexenyl-benzene is only one of the possible evolution pathways.

EXPERIMENTAL

M.ps were determined on a Büchi apparatus and are uncorrected. IR spectra were taken with a Perkin–Elmer 257 spectrometer and NMR spectra with a Perkin–Elmer Hitachi R 24 (60 MHz) spectrometer (with TMS as internal standard). Mass spectra were recorded as a LKB 9000 spectrometer. Gas chromatographic analyses were performed on a Perkin–Elmer F 11 apparatus equipped with F.I.D. and OV 17 1.5% glass column (1.2 m × 4 mm øi).

The new 2,6 - dibenzyliden - cyclohexanols were obtained from the corresponding 2,6 - dibenzylidene - cyclohexanones[16] according to the procedure described.[3]

2,6 - *Di* - p - *methylbenzylidene* - *cyclohexanol* **6d**. Yield 78%, m.p. 129–30° (hexane-ethyl acetate) ν_{max} (CHCl$_3$) 3580, 3400, 1510 cm^{-1}, ^{1}H NMR (δ, CDCl$_3$), 1.70 (m, 2H, $-CH_2-C\underline{H}_2-CH_2-$), 2.05 (d, 1H, J = 5Hz, $-O\underline{H}$), 2.32 (s, 3H, $Ph-C\underline{H}_3$), 2.60 (m, 4H, $-(CH_2-CH_2-CH_2-)$, 4.65 (d, 1H, J = 5Hz $C\underline{H}OH$), 6.55 (s, 2H, 2 $Ph-C\underline{H}=$), 7.12 (s, 8H, aromatics). (Found: C, 86.59; H, 7.93. $C_{22}H_{24}O$ requires: C, 86.80; H, 7.95%).

2,6 - *Di* - p - *nitrobenzylidene* - *cyclohexanol* **6c**. Yield 46%, m.p. 151–2° (MeOH), ^{1}H NMR (δ, CDCl$_3$), 1.30 (m, 2H, $-CH_2-C\underline{H}_2-CH_2-$), 2.60 (m, 5H, $-C\underline{H}_2-CH_2-OH_2$ and $-OH$); 4.68 (s, 1H, $-C\underline{H}-OH$), 6.75 (s, 2H, $Ph-C\underline{H}=$), 7.45 (d, 4H, J = 8Hz, aromatics), 8.23 (d, 4H, J = 8Hz, *o*-nitro-aromatics). (Found: C, 65.30; H, 4.93; N, 7.58. $C_{20}H_{18}N_2O_5$ requires: C, 65.56; H, 4.95; N, 7.65%).

1,3-*Dibenzyl-benzenes* **10**. The chosen dibenzylidene-cyclohexanols (0.03 moles) and PyHCl (50 g) were heated in an open flask at 220° (bath temp.) for 30 min. The cooled mixture still molten (above 120°) was poured into water. The residue which was obtained after extraction with ethyl-ether and removal of the solvent, was distilled and then recrystallised from a suitable solvent.

1,3 - *Dibenzyl* - *benzene* **10a**. Yield 45%, m.p. 16° (petrol-ether). (Lit.[4] 16.9–17°).

1,3 - *di* - p - *chlorobenzyl* - *benzene* **10b**. Yield 44%, m.p. 53–54° (petrol-ether); ν_{max} (CHCl$_3$) 1490, 1095, 1020 cm^{-1}; H–NMR (δ, CDCl$_3$), 3.88 (s, 4H, $Ph-C\underline{H}_2-Ph$), 7.15 (m, 12H, arom.) (Found: C, 73.71, H, 4.91 $C_{20}H_{16}Cl_2$ requires: C, 73.41; H, 4.93%).

1,3 - *Di* - p - *methylbenzyl* - *benzene* **10d**. Yield 38%, m.p. 44–45° (EtOH); ν_{max} (CCl$_4$), 1600, 1510 cm^{-1}; ^{1}H–NMR (δ, CDCl$_3$), 2.30 (s, 6H, $C\underline{H}_3-Ph$), 3.88 (s, 4H, $Ph-C\underline{H}_2-Ph$), 7.08 (s, 12H, arom.). (Found: C, 91.97; H, 7.65. $C_{22}H_{22}$ requires: C, 92.26; H, 7.74%). The 2 - benzyliden - 1 - tetralols were obtained from the corresponding 2 - benzyliden - 1 - tetralones[16] according to the procedure described in reference 3.

2 - p - *Cyano* - *benzylidene* - 1 - *tetralol* **7e**. From 2 - *p* - cyano - benzylidene - 1 - tetralone[16] yield 70%, m.p. 122–24° (95° EtOH); ^{1}H–NMR (δ, CDCl$_3$), 2.80 (m, 5H, $=C-C\underline{H}_2-C\underline{H}_2-C= + -O\underline{H}$), 5.20 (s, 1H, $C\underline{H}-OH$), 6.73 (s, 1H, $-C\underline{H}=$), 7.20–7.70 (m, 8H, arom.). (Found: C, 82.47; H, 5.79; N, 5.54; $C_{18}H_{15}NO$ requires: C, 82.73; H, 5.79; N, 5.36%).

2 - o - *Methyl* - *benzylidene* - 1 - *tetralol* **7f** was obtained, in quantitative yield, from 2 - *o* - methyl - benzylidene - 1 - tetralone[17] as uncrystallisable material which decomposed on heating: ^{1}H–NMR confirmed its structure (δ, CCl$_4$), 2.18 (s, 3H, $Ph-C\underline{H}_3$), 2.65 (m, 5H $=C-C\underline{H}_2-C\underline{H}_2-C= + O\underline{H}$), 4.98 (s, 1H, $C\underline{H}-OH$), 6.55 (s, 1H, $Ph-C\underline{H}=$), 6.90–7.45 (m, 8H, arom.).

Glc/mass analysis of the aromatisation mixture from **7a**. Compd. **7a**[5] (11.7 g) and PyHCl (58 g) were heated at 220° for 15 min, the still warm mixture was poured into water and the oil which separated, was extracted with ethyl-ether. After removal of the solvent, the residue was distilled to give an oil (10 g), b.p. 150° (0.5 mmHg), which showed in glc/mass analysis (1.5% OV 17 on Chromosorb W 80–100 mesh, T = 230°C) five peaks with the following mass spectra:

peak A *m/e* (relative intensity) 220 (M$^+$, 28), 129 (100), 91 (21), corresponding to a dihydrobenzyl-naphthalene.
peak B 218 (M$^+$, 100), 203 (19), 202 (24), 141 (21), 127 (5), 91 (11), corresponding to 2-benzyl-naphthalene.
peak C 218 (M$^+$, 100), 203 (27), 202 (35), 121 (9), 108 (19), 104 (18), corresponding to 7H-5,6-dihydro-benzo/c/fluorene.
peak D 234 (M$^+$, 6), 216 (100), 215 (58), 205 (9), 189 (9), 121 (9), 105 (16), 78 (15) corresponding to 2-benzylidene-1-tetralone (*Z* isomer).
peak E 234 (M$^+$, 60), 216 (100), 215 (70), 206 (65), 205 (90), 191 (20), 189 (20), 178 (20), 232 (40), 105 (60), 103 (40), 91 (23), 78 (60), corresponding to 2-benzylidene-1-tetralone (*E* isomer).

Action of PyHCl on 2-*benzylidene* - 1 - *tetralols* **7**. The chosen benzylidene tetralol (0.03 mol) and PyHCl (50 g) were heated in an open flask at the temp and time reported in the Table 1. The cooled mixture still molten (above 120°) was poured into water. The residue which was obtained after extraction with ethyl ether and removal of the solvent was analysed in glc on OV$_{17}$ column at 230° and then recrystallised or distilled.

In the case of **11a** the product was isolated, after distillation, as picrate. The corresponding benzyl-naphthalenes were obtained from **7a**, **b**, **c**, **d**, the 7H - 5,6 - dihydro - 8 - methyl - benzo/c/fluorene from **7f**, only tars from **7c**.

2 - p - *Chlorobenzyl* - *naphthalene* **11b**. Glc analysis of the crude mixture showed a major peak corresponding to B due to 2 - *p* - chlorobenzyl - naphthalene, a peak corresponding to A and only traces of peaks corresponding to C, D and E. B.p. 190° (0.5 mmHg), m.p. 50–51° (from petrol-ether) (Lit.[8] = 51–52°).

2 - p - *Methylbenzyl* - *naphthalene* **11d**. Glc analysis of the crude mixture showed a major peak corresponding to B due to 2 - *p* - methylbenzyl - naphthalene and traces of peaks corresponding to C, D and E. B.p. 175° (0.5 mmHg), m.p. 54.5–56° (from 95° EtOH) (Lit.[8] 55–6°).

2 - p - *Cyanobenzyl* - *naphthalene* **11e**. Glc analysis of the crude mixture showed only one peak. M.p. 111–114° from hexane-EtOAc, ^{1}H–NMR (δ, CDCl$_3$), 4.18 (s, 2H, $-C\underline{H}_2$), 7.05–7.85 (m, 11H, arom.); IRν_{max} (CHCl$_3$) 2230 cm^{-1}. (Found: C, 88.62; H, 5.38; N, 5.88. $C_{18}H_{13}N$ requires: C, 88.86; H, 5.39; N, 5.76%).

7H-5,6 - *Dihydro* - 8 - *methyl* - *benzo/c/fluorene* **12**. The crude mixture from **7f** showed, in glc analysis, a major peak corresponding to C and other prominent peaks corresponding to A, B, D and E. Two recrystallisations from hexane-EtOAc 7:3 afforded **12** (yield 25%), m.p. 137–9°; ^{1}H–NMR (δ, CDCl$_3$), 2.32 (s, 3H, $C\underline{H}_3-Ph$), 2.74 (m, 4H, $C\underline{H}_2-CH_2$), 3.31 (s, 2H, $=C\cdot C\underline{H}_2-C=$), 6.85–7.85 (m, 7H, arom.). (Found: C, 93.06; H, 6.94. $C_{18}H_{16}$ requires C, 93.10; H, 6.89%).

NaBH$_4$ *reduction of* 2,6 - *dicyclohexenyl* - *cyclohexanone*. To a suspension of 2,6 - dicyclohexenyl - cyclohexanone[12] (6.7 g) in MeOH (50 cc) NaBH$_4$ (about 1 g) was added, at room temp., until no more starting product was present in tlc analysis (hexane-EtOAc 9:1).

The mixture was poured into water and extracted with ether: after removal of the solvent the residue (6 g) showed in tlc two spots. A column chromatographic separation on silica gel (eluent: hexane-EtOAc 9.5:0.5) afforded two isomeric dienols **8** and **9** with R_f values of 0.6 and 0.5 respectively.

(a) 1α, 2a, 6α - 2,6 - *dicyclohexenyl* - *cyclohexanol* **8** (R_f = 0.6; 2 g). Undistillable oil. ^{1}H–NMR (δ, CCl$_4$), 1.12 (s, 1H, $-O\underline{H}$), 1.46–2.20 (m, 24 H), 3.81 (s, 1H, $CH-OH$) 5.50 (s, 2H, $CH_2-C\underline{H}=C$); IR (CCl$_4$), ν_{max} 3560 cm^{-1}. (Found: C, 82.22, H, 10.99. $C_{18}H_{28}O$ requires: C, 82.02; H, 10.84%)

On the basis of its NMR spectrum, the structure **8** was assigned. The singlet at 3.81 (-C$\underline{H}$-OH) indicates that there is no coupling between the carbinol methine proton and the vicinal ones (axial-equatorial relationship).[13]

(b) 1α, 2β, 6β - 2,6 - dicyclohexenyl - cyclohexanol **9** ($R_f = 0.5$; 1 *g*). Undistillable oil.

^{1}H-NMR (δ, CCl_4), 1.10–2.20 (m, 25 H), 3.27 (t, 1H, J = 9 Hz, C$\underline{H}$-OH), 5.50 (s, 2H, $-CH_2-C\underline{H}=C$); IR (CCl_4) ν_{max} 3555 cm^{-1}. (Found: C, 82.85; H, 11.01. $C_{18}H_{28}O$ requires: C, 83.02, H, 10.84%). The triplet at 3.27 with J = 9 Hz relevant to the carbinol methine proton indicates a diaxial coupling and thus a *trans*-relationship between the OH and the two cyclohexenyl groups.[13]

m - *Dicyclohexyl - benzene.* Compound **9** (1 g) and PyHCl (5 g) were heated for 6 hr at 230° until no more starting product was present in tlc (hexane-EtOAc 9:1).

The mixture was poured into water and extracted with ether: after removal of the solvent, the residue was distilled to give *m*-dicyclo-hexyl benzene, 0.5 g, b.p. 150° (0.5 mmHg) (Lit.[18] = 210–12°, 18 mmHg); ^{1}H-NMR (δ, $CDCl_3$), 1.4–2.9 (m, 22 H), 7.0–7.4 (m, 4H, arom.).

Compound **8** (1 g) and PyHCl were treated for 6 hr at 230°; from the mixture worked up as above, a residue was obtained which showed in glc the presence of *m*-dicyclohexyl-benzene and several other unidentified peaks. No effort was made to obtain *m*-dicyclohexyl-benzene as a pure compound.

REFERENCES

[1] Note IV—L. Baiocchi, M. Bonanomi, M. Giannangeli and G. Picconi, *Synthesis* **6**, 434 (1979).

[2] G. Palazzo and L. Baiocchi, *Tetrahedron Letters* 4739 (1968).

[3] G. Hesse, E. Bayer and P. Thieme, *Chem. Ber.* **99**, 1810 (1966).

[4] Paul A. Cantor, *J. Chem. Eng. Data* **8**(3), 459 (1963).

[5] Sekio Mitsui, Yasuhisa Senda and Hideyo Saito, *Bull. Chem. Soc. Japan* **39**, 694 (1966).

[6] Roux, *Ann. Chim. Phys.* (6) **12**, 326 (1877).

[7] N. S. Pivenko, Y. D. Orlov, I. A. Borovoi and V. F. Lavrushin, *Zh. Org. Khim* **10**, 1236 (1974).

[8] M. Z. A. Badr and W. J. Hickinbottom, *J. Chem. Soc.* 4101 (1965).

[9] 1-benzyl and 2-benzyl-naphthalene show the same r.t. on the OV_{17} column described in the experimental. Nevertheless we carefully investigated the presence of the 1-isomer in the crude aromatisation mixture with a 16% PEGA column, on which the two isomers are easily separated, but no 1-isomer was detected.

[10] Graebe, *Chem. Ber.* **27**, 954 (1894).

[11] Graebe assigned the molecular formula $C_{17}H_{12}$ also to the pyrolisis product of 1-benzyl-naphthalene. This formula was corrected by Schroll and Seer to read $C_{17}H_{14}$. *Chem. Ber.* **44**, 1672 (1911).

[12] Iaromir Plesek, *Chem. Listy* **50**, 252 (1956).

[13] See the NMR spectra and the discussion reported by M. Raban, S. K. Lauderback and D. Kost, *J. Am. Chem. Soc.* **97**, 5178 (1975).

[14] R. G. Melton, E. J. Eisenbraun, P. W. K. Flanagan and M. C. Hamming, *Org. Prep. Proced.* **2**, 37 (1970).

[15] P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.* **78**, 1441 (1956).

[16] O. Azzolina, G. Desimoni, V. di Toro, V. Ghislandi and G. Tacconi, *Gazz. Chim. Ital.* **105**, 971 (1975).

[17] W. S. Rapson and R. G. Shyttleworth, *J. Chem. Soc.* 636 (1940).

[18] Y. Bahurel, G. Descotes and J. Sabadie, *Bull. Soc. Chim. Fr.* **6**, 2313 (1971).