Diphenylpyridylmethyl radicals. Part 1. Synthesis, dimerization and ENDOR spectroscopy of diphenyl(2-, 3- or 4-pyridyl)methyl radicals; bond dissociation enthalpies of their dimers[1,2]

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ortho–ortho hydrogen van der Waals repulsions are the origin of the propeller shape of the triphenylmethyl radical and the main reason for the low bond dissociation enthalpy (BDH) of its dimer 1 (44.8 J mol^{-1}). In order to reduce these steric repulsions (eliminating some aromatic hydrogens), diphenyl(2-, 3- or 4-pyridyl)methyl radicals 2–4 were prepared through reductive dehalogenation of the corresponding triarylchloromethanes 2–4a with silver in benzene. They form α,p-dimers 2–4e exclusively through the pyridine ring. ENDOR spectroscopy shows that the structure of the radicals, does not deviate substantially from that of the parent radical, Ph$_3$C$^\bullet$. In contrast, the BDH values of the dimers (measured using EPR spectroscopy) show strengthening of the central C–C bond in 2e (88.7 kJ mol^{-1}) and 3e (90.0 kJ mol^{-1}) and a similar value for 4e (46.4 kJ mol^{-1}) with respect to the trityl dimer 1. This is a consequence of the ground state stabilization of the dimers 2–4e due to relief of strain (elimination of ring hydrogens), whereas in the case of 4e, this stabilization is probably compensated by the formation of a weaker C–N bond with respect to the C–C bond. The above dimers undergo easy 1,5-H-rearrangement, autocatalysed by the basic pyridyl groups themselves.

In general, triarylmethyl compounds are propeller-like in shape owing to the ortho–ortho van der Waals repulsions of adjacent phenyl rings.[3] Particularly, in Gomberg's triphenylmethyl radical[4] the propeller twist[5,6] of ca. 35° seems to be the best compromise between the conflicting[6] requirements for minimum steric repulsion and maximum resonance stabilization.

These steric repulsions and the propeller conformation prevent trityl radicals from combining to give hexaphenylethane (α,α-dimer), a still unknown compound;[7] the less sterically crowded α,p-dimer 1 (Jackobson's structure)[7] is the actual product.[8] α,p-Dimerization seems to be a common[9] way for triarylmethyl radicals[10] to combine as well as for overcrowded diphenylmethyl radicals.[8a,11]

A second important consequence of the above steric interactions is their contribution to the drastic decrease in the bond dissociation enthalpy (BDH) of the a,p-dimer 1 (44.8 kJ

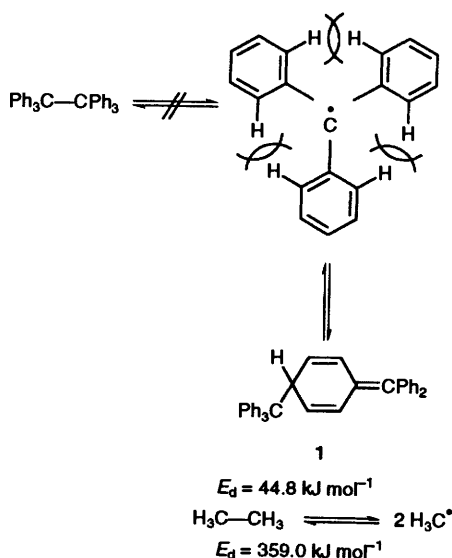E_d = 44.8 kJ mol^{-1}

H_3C—CH_3 ⇌ 2 $H_3C^\bullet$

E_d = 359.0 kJ mol^{-1}

mol^{-1})†,[10] compared with that of the unsubstituted ethane (359.0 kJ mol^{-1}),[12] as suggested a long time ago by Ziegler;[13] the 314 kJ mol^{-1} difference cannot be ascribed alone to the resonance stabilization effect of the trityl radical, as was assumed for many years.[14] Rüchardt and Beckhaus[15] have succeeded in separating quantitatively the contributions of the steric and resonance effects on the bond strength of substituted ethanes. Thus approximately two-thirds of the 314 kJ mol^{-1} decrease in the BDH of the dimer 1 arises from the resonance stabilization of the trityl radical and one-third from the ground-state destabilization of the dimer due to the steric effect. The BDH of the real hexaphenylethane should be even less[16] than 44.8 kJ mol^{-1} and must not be confused with that of the α,p-dimer 1 as usually happens.

The above facts prompted us to undertake the synthesis of the radicals 2–4, replacing one phenyl group of the trityl radical by one pyridyl group (2-Py, 3-Py, 4-Py, respectively) and to study their dimerization products. Elimination of aromatic hydrogens should reduce some steric repulsions and induce relief of strain on the radicals and/or their dimers, e.g., in radical 2 an ortho-hydrogen is removed, thus reducing the ortho–ortho repulsions and probably allowing a greater co-planarity of the aromatic rings compared with the trityl radical. Possible non-bonding interactions between hydrogens and nitrogen lone pairs should not be important as we can conclude by comparing the conformational structure of biphenyl[17] and 2,2'-bipyridine.[17] Whereas biphenyl adopts a twisted conformation due to steric interactions of the ortho-hydrogens, 2,2'-bipyridine shows a planar one; non-bonding interactions between the ortho-hydrogen and the nitrogen lone pair are unimportant here.
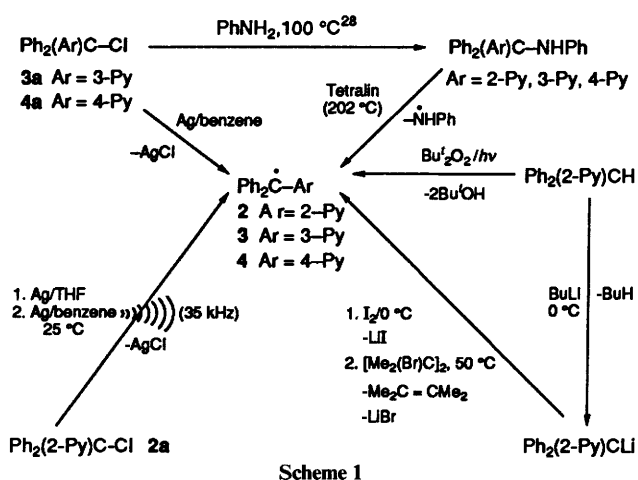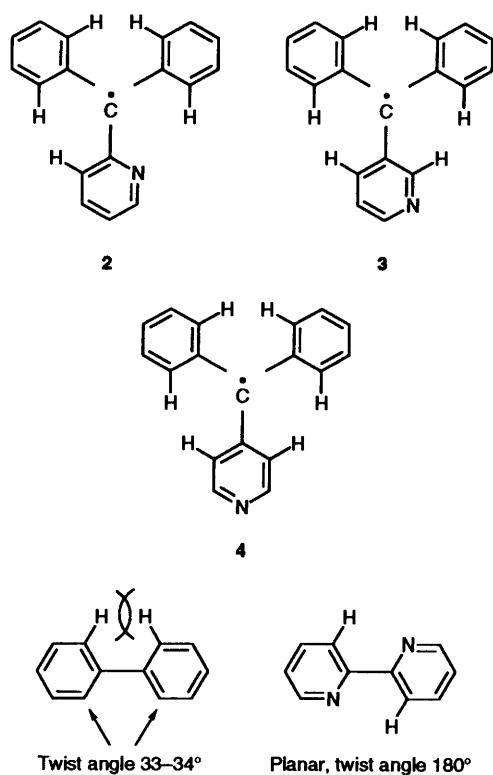
Results and discussion

Radicals 2–4

Radicals 3 and 4 have been prepared by Gomberg's reductive dehalogenation (Scheme 1). Thus, chlorides 3–4a treated with

† 1 cal = 4.184 J.

2 **3**

4

Twist angle 33–34° Planar, twist angle 180°

Scheme 1

Fig. 1 EPR spectrum of radical $Ph_2(3-Py)C^\cdot$ (3) in toluene at 23 °C

with high g-values (2.0297–2.0851), which indicate complex formation; it is known[27] that the diphenyl(2-pyridyl)methane ligand yields very interesting tetrameric cubane clusters with Cu^I.

Radical 2 has also been prepared by the oxidation of the carbanion $Ph_2(2-Py)C^-$ with I_2 or with the dibromide $[Me_2(Br)C-]_2$ or photolytically generated from the diphenyl(2-pyridyl)methane with $Bu^t_2O_2$.

All the radicals 2–4 were also formed by the thermolysis[28] of $Ph_2(Ar)C-NHPh$ (Ar = 2-Py, 3-Py, 4-Py) in tetralin at 202 °C. Weak, but clear EPR spectra of 2–4 have been recorded in this way.

Chloromethanes 2–4a have been prepared using common organometallic reagents and methods.[10a,b,29] Starting from benzophenone, $Ph(3-Py)C=O$ or $4-PyCO_2Et$ and PhLi, 2-PyLi or 3-PyLi, we have synthesized the triarylmethanols 2–4b which are converted to the chlorides 2–4a by the action of $SOCl_2$–AcCl (Scheme 2). It is essential to keep the reaction temperatures low

Scheme 2

silver at room temperature afforded the corresponding radicals 3 and 4; the dehalogenation was completed (Beilstein test)[10a,18,19] in 58 and 180 h, respectively. In contrast, chloride 2a does not lead to radical 2 under the same reaction conditions; however, this was achieved using ultrasonic waves[20,21] (35 kHz) or replacing benzene as a solvent by the more polar tetrahydrofuran.[22]

The reaction times of the three chloromethanes with silver probably reflect their ease of heterolyic fission to $Ph_2(Ar)C^+$ and Cl^-: Ph_3C-Cl[23] > 3a > 4a > 2a. This dissociation, followed by electron transfer from silver to the carbocation, seems to be rate determining, thus supporting the predissociation model[24] of the reductive dehalogenation mechanism of triarylmethyl chlorides.

Our choice in using various suitable metals for the reductive dehalogenation procedure was quite limited by the fact that the pyridyl group constitutes an excellent ligand for the formation of complexes, e.g. chloromethanes 2–4a treated with Cu, probably the most commonly used metal,[10a,b,25,26] lead (at 70 °C, benzene) to precipitates showing very broad EPR spectra
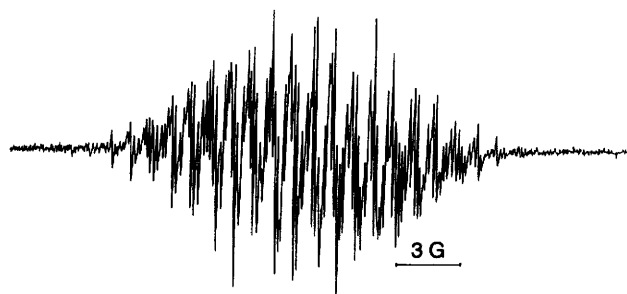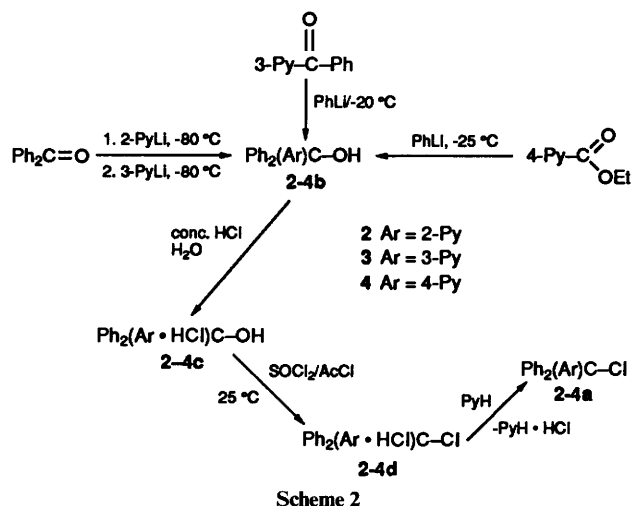
enough (see Scheme 2) to avoid formation of side products which hinder or make the reaction sequence impossible to be carried out. Many preparation procedures mainly described by Wibaut and Otto[29] have been checked and improved in order to become reproducible (see Experimental).

EPR/ENDOR spectroscopy of radicals 2–4

The EPR spectra of the radicals 2–4 have been recorded; they show the anticipated complexity (compared with $Ph_3C^\cdot$) caused by the 1 : 1 : 1 nitrogen splitting and the extra coupling constants arising from the unsymmetrical nature of the molecules (Fig. 1). As these complex EPR spectra could not be analysed in detail, the ENDOR spectroscopy has been applied which allows the investigation of systems with many inequivalent nuclei.[5d,30] Good quality ENDOR spectra of the radicals 3 and 4 were recorded (Fig. 2) and the derived coupling constants are

Table 1 ENDOR data for radicals 2–4 and BDH values (E_d) for their dimers 2–4e

Radical	$a(H)/G^a$	g-Value	Dimer	E_d/kJ mol^{-1}	Temperature interval/°C
Ph$_3$C$^•$	1.14, 2.61 2.86	2.0026	1	44.8 ± 0.8	—
2	b	2.0026	2e	88.7 ± 4.2	−16–15
3	1.15, 2.59 2.80, 2.93	2.0027	3e	90.0 ± 4.6	−27–12
4	0.89, 1.13 2.54, 2.61	2.0029	4e	46.4 ± 2.9	−25–15

^{a} 1 G = 0.1 mT. ^{b} Could not be measured.
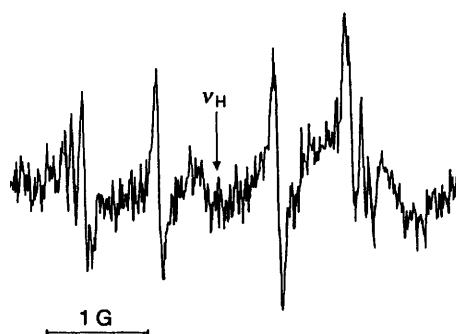
Fig. 2 ENDOR spectrum of radical Ph$_2$(3-Py)C$^•$ (3) in toluene at −3 °C

Scheme 3

displayed in Table 1 along with those of the trityl radical for comparison. The coupling constants of 3 and 4 are close to those of Ph$_3$C$^•$, although it is impossible to assign them precisely. However, taking into account the suggestion that pyridylmethyl radicals are less delocalized than the benzyl radical,[31] we could assign tentatively the larger splittings to the phenyl hydrogens and the smaller to pyridyl keeping always the order $a_p > a_o > a_m$. So, we can assign to radical 3: $a(H_o)$ 2.59, $a(H_m)$ 1.15, $a(H_p)$ 2.93 (phenyl protons), $a[H(2)]$ 2.59, $a[H(4)]$ 2.80, $a[H(5)]$ 1.15 G (pyridyl protons); for radical 4; $a(H_o)$ 2.54, $a(H_m)$ 1.13, $a(H_p)$ 2.61 (phenyl protons), $a[H(2)]$ 2.54, $a[H(3)]$ 0.89 G (pyridyl protons). The constant value of the ratio $|\rho_p/\rho_m| \approx 2.43$ indicates[54,11c,32] the same degree of twisting for every aromatic ring in 3 and 4. The deviation from the co-planarity should be close to that of Ph$_3$C$^•$ ($\rho_p/\rho_m = 2.51$) as one would anticipate since the nitrogen occupies the 3 and 4 position of the ring. In contrast, in the case of radical 2 one should expect a smaller degree of twisting due to the absence of an *ortho*-hydrogen. Actually a greater co-planarity has been found for the perchlorodiphenyl(2-pyridyl)methyl radical compared with perchlorotriphenylmethyl.[33] Unfortunately no ENDOR spectrum could be recorded for 2, but from the same total spectrum width for all three radicals we can assume that the twisting should not be very different. Radicals 2–4 have g-values typical for C-centred free radicals.

Dimerization products of radicals 2–4

Radicals 2–4 form the Jackobson dimers (2–4e) (Scheme 3). From these only 4e has been isolated as a fully characterized crystalline compound. In contrast, instead of the dimers 2e and 3e their 1,5-H-rearranged products 2f and 3f have been isolated. Similarly, if we heated 4e at 70 °C or if we treated 4a with silver at 60–65 °C for 40 h, only 4f was isolated. Obviously a catalysed 1,5-H-rearrangement is responsible for the formation of the benzhydryl derivatives 2–4f since it is well known that Gomberg's dimer (1) or other analogues can be converted through acid-[10c,11b,d,34] or base-[8b,11b,22,35] catalysed 1,5-H-rearrangement to the *p*-benzhydryltetraphenylmethane isomer.
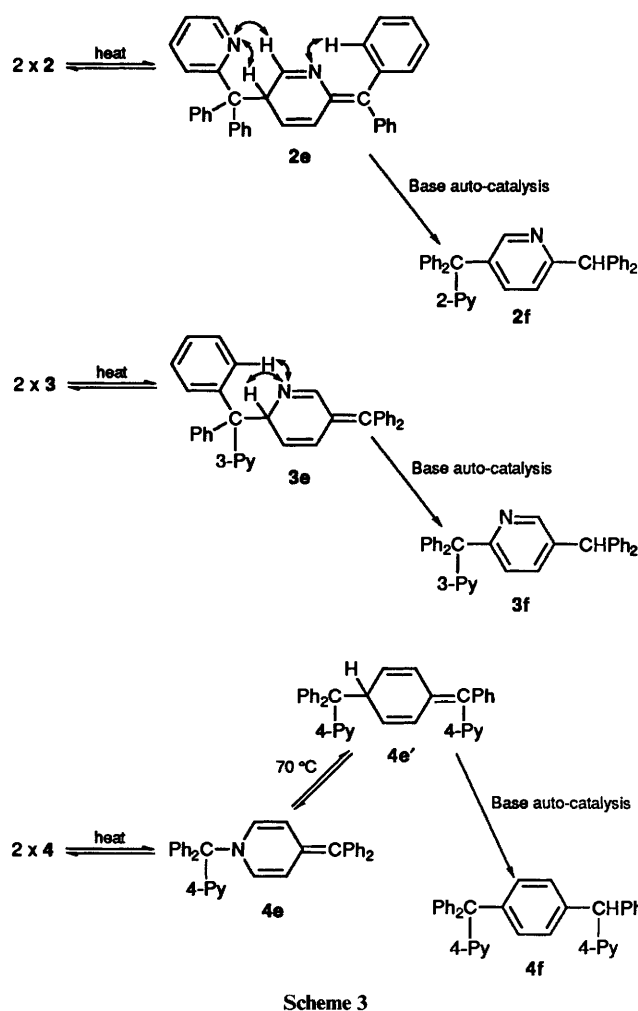
In our isomerization we do not have any acid present, but the pyridyl groups could act as bases autocatalysing the isomerization. This could be clearly demonstrated by the addition of pyridine to a benzene solution of the trityl dimer 1: the intensity of the EPR spectrum of Ph$_3$C$^•$ slowly decreased and after 24 h at 70–75 °C the *p*-benzyhydryltetraphenylmethane isomer was isolated eqn. (1). In the literature, one can find scattered reports about amine-catalysed isomerizations of similar systems.[35b–h]

$$1 \xrightarrow{\text{PyH}} Ph_3C–C_6H_4–CHPh_2 \qquad (1)$$
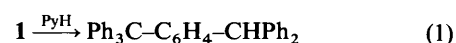
We do not confirm Wibaut's[29] failure to observe radical 3 in a similar experiment. On the other hand because he used pyridine as a solvent, the aforementioned base-catalysed

rearrangement takes place leading to **3f**, the formation of which is now explicable.

The α,p-dimerization of the radicals to **2–4e** seems to proceed exclusively through the pyridyl group. ^{13}C NMR spectroscopy shows a quarternary carbon (*ipso*-pyridyl carbon) at 162.1 ppm, typical for carbon atoms neighbouring the pyridyl nitrogen.[36] Similarly, in **2f** the tertiary carbon at 152.6 ppm could be assigned only to a carbon next to the nitrogen of the 1,4-disubstituted pyridyl ring. ^{1}H NMR spectra are in accord with these structures. ^{1}H NMR spectroscopy of dimer **4e** shows a clear AB-system due to the four cyclohexadienyl protons (the double allylic proton is absent); UV ($\lambda_{max} = 366$ nm, $\varepsilon = 21\,000$ dm^3 mol^{-1} cm^{-3})[8a,37,38] and IR ($v = 1658$ cm^{-1})[11b,35e] data are typical of such systems. The preferential dimerization through the pyridyl ring is probably kinetically and thermo-dynamically controlled, *i.e.* it requires less activation energy, which is not unlikely in view of the less strained (more stable) dimers **2–4e** being formed; the arrows in Scheme 3 indicate the steric repulsions which are absent here owing to the elimination of aromatic hydrogens by the pyridyl nitrogens. In the case of the dimer **4e**, the absence of the double allylic hydrogen of the cyclohexadienyl system makes it resistant to the aforementioned base-autocatalysis, to autoxidation[7a,11b,34e,37] (**4e** represents the first such air-stable dimer) and relieves it from steric strain. However, heating **4e** at 60 °C for 24 h leads to the formation of the rearranged dimer **4f**, which we can confirm from the ^{1}H and ^{13}C NMR spectra; obviously, heat enables dimerization of **4e** to the more strained **4e′** (higher activation energy) which now possesses a double allylic hydrogen and undergoes the abovementioned base-autocatalysed 1,5-H-rearrangement to **4f** irreversibly.

The decreased spin density delocalized on the pyridyl groups in **2–4** compared with the phenyl rings seems to play a minor role for the α,p-dimerization, supporting the suggestion[39] that spin density distribution contributes little to the activation energy in radical recombination reactions. However, the interesting discussion hereupon will continue in view of new results regarding radical recombination (*p,p*-dimerization of tris(2-thienyl)methyl radicals[40] or oxidation of triarylmethyl radicals[41] through the *para*-position).

Bond dissociation enthalpies of 2–4e

The rate of the above rearrangement is negligible when the temperature is kept relatively low ($T < 15$ °C), so that a reversible radical–dimer equilibrium is attained in the temperature range -27–15 °C (see Table 1) which we could show using EPR spectroscopy. Based on these equilibria and using EPR[11b,42] spectroscopy the BDH values of dimers **2–4e** listed in Table 1 have been measured. Note that the BDH values of the dimers **2e** and **3e** are *ca.* 42 kJ mol^{-1} larger than that of the trityl dimer **1**. Supposing that Ph$_3$C·, **2** and **3** are stabilized approximately to the same extent, not unreasonable in view of the above discussion, we are forced to attribute the 42 kJ mol^{-1} increase of the BDHs to the ground state stabilization of the dimers **2e** and **3e**. This is reasonable if we look at space-filling models: elimination of aromatic hydrogens causes relief of strain in the dimer ground state (see arrows in Scheme 3). In the case of dimer **4e**, the relief of strain due to the absence of the double allylic hydrogen causes ground state stabilization, which is probably compensated by the fact that a much weaker bond is formed [E_d(C–N) 289–314 kJ mol^{-1}, *cf.* E_d(C–C) 347–356 kJ mol^{-1}].[43]

The relief of strain does not change the type of the dimerization; it remains an α,p-dimerization.[44] However, it is very interesting to see how the system behaves when a second or even a third phenyl ring of Ph$_3$C· is replaced by further pyridyl groups. Work is in progress in that direction.

Experimental

Ag (powder, 5–8 μm, 99.9%), bromopyridine, benzoylpyridine, Py–CO$_2$Et and diphenyl(2-pyridyl)methane were purchased from Aldrich. All materials were purified before use by distillation or recrystallization and the reactions were carried out under dry argon.

The melting points (uncorrected) were determined with a Büchi 510 instrument; IR spectra, Perkin-Elmer 783 B; ^{1}H and ^{13}C NMR spectra by a Varian EM 390 A and a Brucker AM 300, respectively. Mass spectra, Finnigan Mat 8230, 70 eV; elemental analyses, Carlo Erba 1106 analyser; EPR, Varian E-109 spectrometer; ENDOR, Brucker ER 220 D spectrometer with resonator EN 801.

General procedures

Preparation of alcohols, 2b–4b. *Method A.*—A solution of bromopyridine (20 mmol) in diethyl ether (20 cm^3) was added dropwise to 21 mmol of BuLi (in 30 cm^3 diethyl ether) at -78 °C and over a period of 1.5 h. Stirring was continued for another hour. A solution of benzophenone (20 mmol) in diethyl ether (15 cm^3) was added slowly to the reaction mixture, while the temperature was kept at -78 °C. The mixture was stirred at -78 °C for 2 h, allowed to warm to room temperature and treated with dilute HCl (1.3 mol dm^{-3}; 25 cm^3). The ether layer was separated and extracted with HCl (1.3 mol dm^{-3}; 2 × 10 cm^3). The combined aqueous extracts were washed with diethyl ether (3 × 10 cm^3), neutralized with saturated aq. NaHCO$_3$, made alkaline (pH 9–10) with NaOH (1 mol dm^{-3}) and extracted again with diethyl ether (3 × 15 cm^3). The ether extracts were washed with H$_2$O (2 × 10 cm^3), dried (Na$_2$SO$_4$) and filtered. The ether was evaporated and the residue (alcohol) recrystallized from various solvents. The alcohols were white crystalline compounds.

Method B.—A solution of 41 mmol of PhLi in diethyl ether (25 cm^3) was added dropwise to a solution of benzoylpyridine (40 mmol) in 10 cm^3 of diethyl ether at -10 °C and within 1 h. Stirring was continued for 2 h at the same temperature, the reaction mixture was allowed to warm to room temperature and treated with dilute HCl (1.3 mol dm^{-3}) as described by method A.

Method C.—A solution of 31 mmol of PhLi in diethyl ether (40 cm^3) was added to a solution of Py–CO$_2$Et (15 mmol) in diethyl ether (20 cm^3) at -25 °C. The reaction mixture was stirred at the same temperature for an additional 2 h and treated with dilute HCl (1.3 mol dm^{-3}) as described by method A.

Preparation of the hydrochloric salts Ar$_3$COH·HCl (2c–4c). A suspension of **2b–4b** (4 mmol) in 10 cm^3 of water was treated with 1 cm^3 of conc. HCl. The reaction mixture was refluxed for 1 h and then allowed to cool to room temperature. The water was removed under reduced pressure (12 Torr at 40 °C) and the white residue crystallized by the addition of ether and dried *in vacuo* (5 mTorr‡) at 40 °C for 2 h.

Preparation of the hydrochloric salts Ar$_3$CCl·HCl (2d–4d). A solution of **2c–4c** (3.4 mmol), 6 cm^3 of SOCl$_2$ and 4 cm^3 of AcCl (both freshly distilled) was stirred at room temperature for 48 h. The excess SOCl$_2$ and AcCl was removed at room temperature under reduced pressure (12 Torr). Heat led practically to decomposition. The residue was crystallized by the addition of benzene (with the exclusion of moisture).

Preparation of radical precursors Ar$_3$CCl (2a–4a). A suspension of **2d–4d** (1 mmol) in 15 cm^3 benzene and 0.3 cm^3 pyridine was stirred at room temperature for 1 h. The white precipitate (pyridine hydrochloride) was filtered and the filtrate was evaporated. The white residue was crystallized by the addition of hexane.

‡ 1 Torr = 133.32 Pa.

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Hydrolysis of **2a–4a** (30 min stirring with H_2O) afforded *ca.* 95% yield of the hydrochloric salts **2c–4c** of the alcohols.

Preparation of radicals 2 and 4 and their dimers. A solution of **3a** or **4a** (2 mmol) in 15 cm^3 of carefully dried and degassed benzene was stirred under argon with a ten-fold excess of Ag at room temperature until the Beilstein test proved negative. Exclusion of light was also necessary in order to avoid disproportionation. The EPR signals of the radicals **3** and **4** were recorded from the yellow coloured solution. AgCl and excess Ag were filtered off and the filtrate was evaporated and reduced in volume by *ca.* 30%. Hexane was added slowly until the solution started to become turbid. A light yellow solid was precipitated overnight, filtered and washed with hexane (3 × 5 cm^3). To remove hexane and benzene from the light yellow dimer it was necessary to dry *in vacuo* (5 mTorr) at 40 °C for 8 h.

Diphenyl(2-pyridyl)methanol (2b)
According to the general procedure A from 6.34 g (40 mmol) of 2-bromopyridine, 42 mmol of BuLi and 7.9 g (43 mmol) of benzophenone, 5.44 g (52%) of **2b** was obtained; mp 103–105 °C (methanol) (lit.,[45] 105 °C); ν_{max}(KBr)/cm^{-1} 3350 (OH); δ_H(CD$_3$OD) 7.21–7.28 (11 H, m, Ar*H*), 7.38–7.72 (2 H, m, PyH) and 8.50 (1 H, m, 2-PyH); δ_C(CD$_3$OD) 82.52 (C–OH) and 123.47–165.52 (HC$_{ar}$, C$_{ar}$); m/z 261 (M$^+$, 100%) and 184 (M$^+$ – Ph, 47) (Found: C, 82.85; H, 5.95; N, 5.4. C$_{18}$H$_{15}$NO requires C, 82.73; H, 5.79; N, 5.36%).

Diphenyl(3-pyridyl)methanol (3b)
(*a*) According to the general procedure B from 3.13 g (17.1 mmol) of 3-benzoylpyridine and 22 mmol of PhLi, 2.86 g (64%) of **3b** was obtained. It was crystallized by the addition of diethyl ether; mp 115 °C (lit.,[46a] 119–120 °C; lit.,[46b,c,29] 115 °C); ν_{max}(KBr)/cm^{-1} 3090 (OH, C–H$_{ar}$); δ_H(CD$_3$OD) 7.22–7.33 (10 H, m, ArH), 7.36, 7.71 (2 H, m, PyH) and 8.41 (2 H, m, 2-PyH); δ_C(CD$_3$OD) 81.33 (C–OH) and 124.33–149.76 (HC$_{ar}$, C$_{ar}$); m/z 261 (M$^+$, 18%), 183 (M$^+$ – Py, 88) and 77 (Ph$^+$, 100) (Found: C, 82.6; H, 5.9; N, 5.4).

(*b*) According to the general procedure A from 3.66 cm^3 (38 mmol) of 3-bromopyridine, 40 mmol of BuLi and 6.93 g (38 mmol) of benzophenone, 7.54 g (76%) of **3b** was obtained; mp 113–115 °C.

Diphenyl(4-pyridyl)methanol (4b)
According to the general procedure C from 6.5 g (43 mmol) of ethyl isonicotinate and 90 mmol of PhLi, 8.09 g (72%) of **4b** was obtained after recrystallization from *N,N*-dimethylformamide; mp 233 °C (lit.,[47a] 240–242 °C; lit.,[47b] 235–237 °C); ν_{max}(KBr)/cm^{-1} 3300–2980 (OH, C–H$_{ar}$); δ_H(CDCl$_3$–CF$_3$CO$_2$D) 7.25–7.41 (10 H, m, ArH), 8.12 (2 H, m, PyH) and 8.75 (2 H, m, 2-PyH); δ_C(CDCl$_3$–CF$_3$CO$_2$D) 81.59 (C–OH) and 125.83–167.44 (HC$_{ar}$, C$_{ar}$); m/z 261 (M$^+$, 40%) 184 (M$^+$ – Ph, 23), 183 (M$^+$ – Py, 64) and 105 (PhCO$^+$, 100) (Found: C, 82.65, H, 5.9; N, 5.3).

Diphenyl(2-pyridyl)methanol hydrochloride (2c)
From 2.0 g (7.6 mmol) of **1a** and 0.9 cm^3 of conc. HCl, 2.19 g (96%) of **2c** was obtained; mp 178–180 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3320–2500 (OH, C–H$_{ar}$, NHCl); δ_H(CD$_3$OD–CDCl$_3$) 7.35–7.46 (10 H, m, ArH), 7.93, 8.04, 8.56 and 8.79 (4 H, m, PhH); δ_C(CD$_3$OD–CDCl$_3$) 80.20 (C–OH) and 125.61–159.79 (HC$_{ar}$, C$_{ar}$); m/z 261 (M$^+$ – HCl, 100%) and 184 (M$^+$ – HCl – Ph, 54) (Found: C, 72.4; H, 5.3; N, 4.7. C$_{18}$H$_{16}$ClNO requires C, 72.59; H, 5.42; N, 4.70%).

Diphenyl(3-pyridyl)methanol hydrochloride (3c)
From 7.54 g (28.8 mmol) of **3b** and 2.5 cm^3 of conc. HCl, 6.85 g (80%) of **3c** was obtained; mp 232–234 °C (decomp.) (lit.,[29] 227 °C); ν_{max}(KBr)/cm^{-1} 3215 (OH) and 2900–2200 (NHCl); δ_H(CD$_3$OD) 4.98 (1 H, s, OH), 7.29–7.41 (10 H, m, ArH), 8.04, 8.52 (2 H, m, PyH) and 8.80 (2 H, m, 2-PyH); δ_C(CD$_3$OD) 85.87 (C–OH) and 127.77–150.04 (HC$_{ar}$, C$_{ar}$); m/z 261 (M$^+$ – HCl, 8%), 183 (M$^+$ – HCl – Py, 30) and 105 (PhCO$^+$, 100) (Found: C, 72.5; H, 5.6; N, 4.6).

Diphenyl(4-pyridyl)methanol hydrochloride (4c)
From 3.86 g (14.8 mmol) of **4b** and 1.4 cm^3 of conc. HCl, 4.21 g (96%) of **4c** was obtained; mp 203–205 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3210 (OH) and 2900–2200 (NHCl); δ_H(CD$_3$OD) 7.29–7.40 (10 H, m, ArH), 8.11 (2 H, m, PyH) and 8.80 (2 H, m, 2-PyH); δ_C(CD$_3$OD) 82.18 (C–OH) and 127.14–169.78 (HC$_{ar}$, C$_{ar}$); m/z 261 (M$^+$ – HCl, 76%), 184 (M$^+$ – HCl – Ph, 38) and 105 (PhCO$^+$, 100) (Found: C, 72.6; H, 5.5; N, 4.7).

Diphenyl(2-pyridyl)chloromethane hydrochloride (2d)
From 2.93 g (9.8 mmol) of **2c**, 26 cm^3 of SOCl$_2$ and 15 cm^3 of AcCl, 2.79 g (90%) of **2d** was obtained; mp 145 °C; ν_{max}(KBr)/cm^{-1} 2800–2100 (NHCl); δ_H(CDCl$_3$) 7.18–7.32 (10 H, m, ArH), 7.45, 7.98, 8.46 (3 H, m, PyH) and 9.14 (1 H, m, 2-PyH); δ_C(CDCl$_3$) 76.19 (C–Cl) and 126.24–156.66 (HC$_{ar}$, C$_{ar}$); m/z 279 (M$^+$ – HCl, 2%) and 244 (M$^+$ – HCl – Cl, 100) (Found: C, 68.3; H, 5.0; N, 4.3. C$_{18}$H$_{15}$Cl$_2$N requires C, 68.37; H, 4.78; N, 4.43%).

Diphenyl(3-pyridyl)chloromethane hydrochloride (3d)
From 3.5 g (11.7 mmol) of **3c** 26 cm^3 of SOCl$_2$ and 17 cm^3 of AcCl, 3.15 g (85%) of **3d** was obtained; mp 150–152 °C (lit.,[29] 150–152 °C); ν_{max}(KBr)/cm^{-1} 2850–2130 (NHCl); δ_H(CDCl$_3$) 7.14–7.44 (10 H, m, ArH), 8.01, 8.45, 8.87 (4 H, m, PyH) and 18.42 (s, 1 H, NH); δ_C(CDCl$_3$) 76.73 (C–Cl) and 126.21–146.60 (HC$_{ar}$, C$_{ar}$); m/z 244 (M$^+$ – HCl – Cl, 36%) and 78 (Py$^+$, 100) (Found: C, 68.1; H, 4.7; N, 4.4).

Diphenyl(4-pyridyl)chloromethane hydrochloride (4d)
From 2.96 g (9.9 mmol) of **4c**, 26 cm^3 of SOCl$_2$ and 17 cm^3 of AcCl, 2.66 g (85%) of **4d** was obtained: mp 180 °C (lit.,[47a] 134–135 °C); ν_{max}(KBr)/cm^{-1} 2900–2130 (NHCl); δ_H(CDCl$_3$) 7.14–7.31 (10 H, m, ArH), 7.77 (2 H, m, PyH) and 8.93 (2 H, m, 2-PyH); δ_C(CDCl$_3$) 77.82 (C–Cl) and 127.06–164.11 (HC$_{ar}$, C$_{ar}$); m/z 244 (M$^+$ – HCl – Cl, 100%) (Found: C, 68.4; H, 4.9; N, 4.5).

Diphenyl(2-pyridyl)chloromethane (2a)
From 1.74 g (5.5 mmol) of **2d** and 1.4 cm^3 (17.4 mmol) of pyridine, 1.09 g (71%) of **2a** was obtained; mp 70–72 °C (lit.,[48] 72.3–73.3 °C); ν_{max}(KBr)/cm^{-1} 3080, 3050 (C–H$_{ar}$); δ_H(CDCl$_3$) 7.16–7.63 (13 H, m, ArH, PyH) and 8.7 (2 H, m, 2-PyH); δ_C(CDCl$_3$) 80.6 (C–Cl) and 122.2–162.5 (HC$_{ar}$, C$_{ar}$); m/z 279 (M$^+$, 0.4%), 245 (M$^+$ – Cl, 50 and 243 (M$^+$ – Cl – H, 100) (Found: C, 77.1; H, 5.25; N, 5.0. C$_{18}$H$_{14}$ClN requires C, 77.26; H, 5.04; N, 5.01%).

Diphenyl(3-pyridyl)chloromethane (3a)
From 2.64 g (8.3 mmol) of **3d** and 2 cm^3 (24.9 mmol) of pyridine, 1.74 g (75%) of **3a** was obtained; mp 80–81 °C (lit.,[29] 80–82 °C); ν_{max}(KBr)/cm^{-1} 3055, 3020 (C–H$_{ar}$); δ_H(CDCl$_3$) 7.20–7.35 (11 H, m, ArH, PyH), 7.60–7.70, 8.49 (3 H, m, heteroaromatic H); δ_C(CDCl$_3$) 78.9 (C–Cl) and 122.7–145.4 (HC$_{ar}$, C$_{ar}$) (Found: C, 76.9; H, 5.1; N, 4.9).

Diphenyl(4-pyridyl)chloromethane (4a)

From 3.2 g (10 mmol) of **4d** and 2.4 cm³ (29.8 mmol) of pyridine, 2.45 g (87%) of **4a** was obtained; mp 83–85 °C (lit.,[47b] 89.5–90.5); ν_{max}(KBr)/cm⁻¹ 3055, 3030 (C–H$_{ar}$); δ_H(CDCl₃) 7.16–7.29 (12 H, m, ArH, PyH), 8.53 (2 H, m, 2-PyH); δ_C(CDCl₃) 79.34 (C–Cl) and 124.94–153.93 (HC$_{ar}$, C$_{ar}$); m/z 280 (M⁺, 9%), 245 (M⁺ − Cl, 100) and 165 (M⁺ − Cl − Py, 37) (Found: C, 77.0; H, 5.2; N, 4.9).

Diphenyl(2-pyridyl)methyl radical (2) and 2-diphenylmethyl-5-[diphenyl(2-pyridyl)methyl]pyridine (2f)

(a) According to the general procedure, from 0.58 g (2.0 mmol) of **2a** and 2.5 (23 mmol) of Ag in 15 cm³ of benzene, 0.38 g (78%) of **2f** was obtained after 24 h at 65 °C; mp 194 °C (decomp.) (acetone); λ_{max}(Et₂O)/nm 266.5 (ε/dm³ mol⁻¹ cm⁻¹ 14 645); ν_{max}(KBr)/cm⁻¹ 3065, 3030 (C–H$_{ar}$) and 2965 (C–H$_{aliph.}$); δ_H(CDCl₃) 5.69 (1 H, s, C–H), 6.88–7.60 (25 H, m, ArH) and 8.50–8.61 (2 H, m, 2-PyH); δ_C(CDCl₃) 58.9 (Ph₂C–H), 64.7 [Ph₂C-(2-Py)] and 121.1–164.5 (HC$_{ar}$, C$_{ar}$); m/z 488 (M⁺, 100%), 487 (M⁺ − H, 57) and 244 (M⁺/2, 26) (Found: C, 88.3; H, 5.9; N, 5.4. C₃₆H₂₈N₂ requires C, 88.49; H, 5.78; N, 5.73%). **2** was not detected by EPR spectroscopy under these conditions. At room temperature no reaction was observed.

(b) A solution of lithium diphenyl(2-pyridyl)methanide[49] [freshly prepared by the addition of 0.3 g (1.2 mmol) of diphenyl(2-pyridyl)methane in diethyl ether (5 cm³) to 1.0 mmol of BuLi in diethyl ether (2.5 cm³) at 0 °C] and a solution of 0.084 g (0.8 mmol) of I₂ in diethyl ether (4 cm³) were added simultaneously to 2 cm³ of diethyl ether at 0 °C. The dark red colour of the anion disappeared immediately and the EPR spectrum of **2** was recorded.

(c) A solution of lithium diphenyl(2-pyridyl)methanide (2.8 mmol) in diethyl ether (5.5 cm³) was added to a solution of 0.37 g (1.5 mmol) of 2,3-dibromo-2,3-dimethylbutane in 5 cm³ of diethyl ether at 0 °C. The dark red colour of the anion disappeared immediately. The mixture was stirred for 2 h at this temperature. The solvent was evaporated and 10 cm³ of benzene was added. The light red solution gave the EPR spectrum of **2** (addition at − 50 °C led to a stronger EPR signal). After two days at room temperature LiBr was precipitated, filtered and the filtrate was evaporated and reduced in volume by ca. 30%. Hexane was added slowly until the solution started to become turbid. The light yellow solid **2f** precipitated overnight and was filtered and washed with hexane (3 × 5 cm³). To remove hexane and benzene from the light yellow dimer it was necessary to dry in vacuo (5 mTorr) at 40 °C for 5 h; yield 0.26 g (38%).

2,3-Dibromo-2,3-dimethylbutane

A solution of 1.7 cm³ (33.0 mmol) of Br₂ in 8 cm³ CCl₄, was added to a solution of 4 cm³ (33.6 mmol) of 2,3-dimethylbut-2-ene in 18 cm³ of CCl₄, at 0–5 °C. The solution was treated with K₂CO₃ overnight. The precipitate was filtered and the filtrate was evaporated. The white product 2,3-dibromo-2,3-dimethylbutane was washed with hexane and drops of diethyl ether. Yield 3.84 g (47%); mp 170 °C (lit.,[50] 190, 177, 169–170 °C); ν_{max}(KBr)/cm⁻¹ 3000, 2980, 2940, 2870 (C–H$_{aliph.}$) and 535–525 (C–Br); δ_H(CCl₄) 2.1 (12 H, s, CH₃).

Diphenyl(3-pyridyl)methyl radical (3) and 5-(diphenylmethyl)-2-[diphenyl(3-pyridyl)methyl]pyridine (3f)

According to the general procedure, from 0.21 g (0.7 mmol) of **3a** and 0.9 g (8.3 mmol) of Ag in 7 cm³ of benzene at room temperature, the EPR spectrum of **3** was recorded and 0.15 g (83%) of **3f** was obtained after 58 h and recrystallization from

hot ethanol and benzene; mp 213 °C (lit.,[29] 217–219 °C). The reaction was performed also at 60 °C taking only **3f** after 5 h; λ_{max}(Et₂O)/nm 263.6 (ε/dm³ mol⁻¹ cm⁻¹ 13 818); ν_{max}(KBr)/cm⁻¹ 3035 (C–H$_{ar}$) and 2960 (C–H$_{aliph.}$); δ_H(CDCl₃) 5.57 (1 H, s, C–H), 7.15–7.37, 7.6–7.7, 8.45 (27 H, m, ArH, PyH); δ_C(CDCl₃) 54.1 (Ph₂C–H) 64.6 [Ph₂C–(3-Py)] and 125.1–162.1 (HC$_{ar}$, C$_{ar}$); m/z 488 (M⁺, 100%), 487 (M⁺ − H, 58) and 244 (M⁺/2, 20) (Found: C, 88.2; H, 6.0; N, 5.4. C₃₆H₂₈N₂ requires C, 88.49; H, 5.78; N, 5.73%).

Diphenyl(4-pyridyl)methyl radical (4) and 1-[diphenyl(4-pyridyl)methyl]-4-(diphenylmethylene)-1,4-dihydropyridine (4e)

According to the general procedure from 0.74 g (2.6 mmol) of **4a** and 3.59 g (33.0 mmol) of Ag in 17 cm³ of benzene at room temperature, the EPR spectrum of **4** was recorded and 0.46 g (73%) of **4e** was obtained after 180 h; mp 108 °C (decomp.); λ_{max}(Et₂O)/nm 288.0 (ε/dm³ mol⁻¹ cm⁻¹ 5500) and 366.0 (21 000); λ_{max}(KBr)/nm 380; ν_{max}(KBr)/cm⁻¹ 1658; δ_H(CDCl₃) 5.98, 6.18 (AB, ³J$_{AB}$ = 8.1 Hz, 4 H$_{alkene}$), 6.87–7.6 (22 H, m, ArH, PyH) and 8.57 (2 H, m, 2-PyH); δ_C(CDCl₃) 110.26 [Ph₂(4-Py)C–N], 125.15, 131.32 (C$_{alkene}$) and 122.76–151.6 (HC$_{alkene}$, HC$_{ar}$, C$_{ar}$); m/z 244 (M⁺/2, 100%) (Found: C, 88.3; H, 5.6; N, 5.4).

1-(Diphenylmethyl)-4-(triphenylmethyl)benzene

We found that the EPR signal of the triphenylmethyl radical was reduced at 75 °C in a benzene–pyridine mixture; 0.24 g (0.5 mmol) of 'hexaphenylethane' **1** in 5 cm³ benzene was stirred with 8 cm³ (98.9 mmol) of pyridine for 24 h at 70–75 °C. The solvents were evaporated and the ¹H NMR (CDCl₃) spectrum of the residue showed the formation of the dimer 1-(diphenylmethyl)-4-(triphenylmethyl)benzene; δ_H(CDCl₃) 5.5 (1 H, s, C–H) and 7.25 (29 H, m, ArH).

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