Selective mono-benzylation of methylene active compounds with dibenzyl carbonate: benzylation of phenol

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Dibenzyl carbonate (DBzlC) has been used to benzylate phenylacetonitrile, benzyl phenylacetate and phenol. In refluxing *N*,*N*-dimethylformamide (DMF) as solvent, and in the presence of K_2CO_3 phenol yielded benzyl phenyl ether and phenylacetonitrile the monobenzylated compound 2,3-diphenylpropionitrile. Likewise, in refluxing *N*,*N*-diethylformamide (DEF), benzyl phenyl acetate gave the benzyl 2,3-diphenylpropionate. Selectivity in mono-*C*-benzyl derivatives was 98–99% at a conversion up to 90%. Such unusually high selectivity is explained in terms of a mechanism involving, initially, carboxybenzylation followed by benzylation, rather than direct benzylation.

Introduction

Although direct *C*-alkylation of methylene active compounds, particularly arylacetonitriles and alkyl arylacetates, may be effected by several methods, alkyl halides and dialkyl sulfates are usually employed as the alkylating agents.[1a–l] However, these reactions have a general drawback in that they are poorly selective and give rise to mixtures of mono- and di-alkylated products. Better results can be achieved under phase-transfer catalysis (PTC) conditions[2a–e] even though, when reactive alkylating agents (*e.g.* methyl, allyl and benzyl halides) are used, mono-alkyl selectivity remains low.[2c–e] For some compounds, other often more complicated, synthetic strategies have also been reported.[1h–i,3a–h]

Recently, we reported that dialkyl carbonates [dimethyl (DMC) and diethyl (DEC) carbonate], once believed completely ineffective for alkylations,[1a] are, in fact, excellent and very selective.[4a–b] In particular, operating both under gas-liquid phase-transfer catalysis (GL-PTC)[5] and batch conditions, at high temperatures (170–220 °C), dialkyl carbonates allow very selective mono-alkylations of arylacetonitriles and alkyl arylacetates [eqn. (1)], the reactions occurring in the presence of a base (usually K_2CO_3).

$$\underset{\mathbf{1}}{ArCH_2X} + ROCO_2R \xrightarrow{base} \underset{\mathbf{2}}{ArCH(R)X} + ROH + CO_2 \quad (1)$$

X = CN (**2a**), CO_2R (**2b**); R = Me, Et

Typically, despite the high temperatures used, mono-alkylation selectivity is > 99.5% (at complete conversion).[6a–c]

Under these conditions, DMC is also very effective in the *O*-alkylation of phenols, to give the corresponding anisoles.[4a,7]

Alkylation by dialkyl carbonates is characterized by the absence of waste and a complete recycling of the co-product alcohol; these features encouraged us to explore the applicability of this new synthetic method.

Results

Here we report the highly selective mono-*C*-benzylation of phenylacetonitrile and benzyl phenyl acetate with dibenzyl carbonate (DBzlC) [eqn. (2)].

$$\underset{\mathbf{1a}}{PhCH_2X} + PhCH_2OCO_2CH_2Ph \xrightarrow{K_2CO_3} \underset{\mathbf{3}}{PhCH(CH_2Ph)X} + PhCH_2OH + CO_2 \quad (2)$$

X = CN (**3a**), CO_2CH_2Ph (**3b**)

At the same time, we report that DBzlC has proved to be a good *O*-alkylating agent of phenol giving the corresponding benzyl phenyl ether [eqn. (3)].

$$PhOH + PhCH_2OCO_2PhCH_2 \xrightarrow{K_2CO_3} \underset{\mathbf{4}}{PhOCH_2Ph} + PhCH_2OH + CO_2 \quad (3)$$

Both *C*- and *O*-benzylations were performed under batch conditions operating at 140–180 °C, in a variety of solvents [*N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF), triethylene glycol dimethyl ether (Triglyme), polyethylene glycol 250 (PEG 250), xylene] and in the presence of a 2 mol equiv. of K_2CO_3. All reactions were carried out under N_2 (atmospheric pressure) in order to prevent the oxidation of the co-product benzyl alcohol to benzaldehyde or other products through Knoevenagel condensation with the reagent substrate [*i.e.* PhC(CN)=CHPh, see Tables 1–2].[1f,3b] *C*- Benzylation of phenylacetonitrile was the more extensively studied reaction.

Table 1 reports the results obtained in the reaction of phenylacetonitrile with DBzlC in the presence of different solvents. Selectivity in the mono-*C*-benzyl derivative (2,3-diphenylpropionitrile, **2a**) was always very high (98–99%) at conversions up to 90%.

Aprotic, polar solvents (DEF, DMF) used at the reflux temperature (155 and 177 °C, respectively), gave the fastest reactions (entries 1–2). Despite the well-known properties of polyethylene glycols as anion activators,[8] the use of Triglyme and PEG 250 resulted in longer reaction times, even operating at 180 °C (entries 3–6). Xylene completely depressed the reaction (entry 7): thus, at the reflux temperature (140 °C), almost no reaction occurred after 3.0 h while at the same temperature, but in DMF, conversion was 43.3% after 5.0 h (entry 1, Table 2).

Table 2 reports the effect of the reaction temperature and the substrate/alkylating agent molar ratio for the benzylation of phenylacetonitrile. Also, a comparison between DBzlC and $PhCH_2Cl$ as alkylating agents is shown. Operating at 120 °C in DMF, only 5% conversion was observed after 3.0 h (entry 1); higher temperatures, up to 140 °C, were required for the reaction to occur at an appreciable rate (entries 1,2). The reaction rate could also be increased by decreasing the substrate/DBzlC molar ratio (entries 2–4), this behaviour appearing even when other solvents were used (compare entries 3,4 and 5,6, Table 1).

The comparison between DBzlC and $PhCH_2Cl$ was made both in DMF (entries 5,6) and under PTC conditions (toluene

Table 1 Benzylation of phenylacetonitrile with dibenzyl carbonate in the presence of different solvents[a]

Entry	Solvent	Reaction time (t/h)	Temp. (T/°C)	Molar ratio[b] (Sub./Alkyl.)	Conv'n (%)	Selectivity[c] (%)	Products (%)[d] PhCH(R)CN	PhC(R_2)CN (R = CH_2Ph)	PhC(CN)=CHPh
1	DEF	1.25	177[e]	1:1.1	91.7	99.1	88.2	0.8	2.7
		1.5	177	1:1.1	98.5	97.9	93.6	2.0	2.9
2	DMF	4.0	155[e]	1:1.1	86.0	99.2	83.5	0.6	1.9
3	Triglyme	2.0	160	1:1.1	8.0				
		6.0	180	1:1.1	62.2	100	60.0	—	2.2
4	Triglyme	8.25	180	1:3.0	93.1	99.5	90.8	0.5	1.8
5	PEG 250	7.25	180	1:1.1	47.5	100	45.0	—	2.5
6	PEG-250	7.0	180	1:3.0	83.0	100	75.5	—	7.5
7	Xylene[f]	3.0	90	1:1.1	—				
		3.0	110	1:1.1	—				
		3.0	140[e]		1.8		0.8	—	1.0

[a] 2 mol equiv. of K_2CO_3 were used in all reactions. [b] $PhCH_2CN$/DBzlC molar ratio. [c] Selectivity is defined as: [PhCH(R)CN]/{[PhCH(R)CN] + [PhC(R_2)CN]} × 100; R = CH_2Ph. [d] Other by-products were $PhCH_2OCH_2Ph$, $PhCOOCH_2Ph$, $PhCH_2COPh$ whose total amount (referred to the main product, PhCH(R)CN) was < 1% (entries 1–4) and ≤7% (entries 5–6). [e] Reflux temperature of the solvent. [f] Aliquat 336 (2% molar with respect to the substrate) was used as phase-transfer catalyst.

Table 2 Benzylation of phenylacetonitrile at different temperatures and molar ratios (substrate to alkylating agent)

Entry*	Solvent	Reaction time (t/h)	Temp. (T/°C)	Alkylating agent	Molar ratio (Sub./Alkyl.)	Conv'n (%)	Selectivity[a] (%)	Products (%)[b] PhCH(R)CN	PhC(R_2)CN (R = CH_2Ph)	PhC(CN)= CHPh
1	DMF	3.0	120	DBzlC	1:1.1	4.8	100			
		5.0	140	DBzlC	1:1.1	43.3	100	41.7	—	1.6
2	DMF	4.0	155	DBzlC	1:1.1	86.0	99.2	83.5	0.6	1.9
3	DMF	2.5	155	DBzlC	1:1.5	91.7	99.1	87.7	0.8	3.2
4	DMF	2.25	155	DBzlC	1:3.0	95.6	98.4	91.7	1.5	2.4
		2.75	155	DBzlC	1:3.0	100	95.1	92.6	4.7	2.7
5	DMF	6.0	40	$PhCH_2Cl$	1:0.8	48.1	84.9	40.6	7.2	0.3
6	DMF	4.0	80	$PhCH_2Cl$	1:1.5	82.3	64.9	52.1	28.2	2.0
7	Toluene[c]	4.0	rt	$PhCH_2Cl$	1:1	18.2	93.4	17.0	1.2	—
		19.5	rt	$PhCH_2Cl$	1:1	81.1	53.1	41.1	36.3	3.7

* Entries 1–6: 2 mol equiv. of K_2CO_3 were used. [a] The selectivity is defined as: [PhCH(R)CN/{[PhCH(R)CN] + [PhC(R_2)CN]} × 100; R = CH_2Ph. [b] Entries 1–4: other by-products were $PhCH_2OCH_2Ph$, $PhCOOCH_2Ph$, $PhCH_2COPh$ whose total amount (referred to the main product, PhCH(R)CN) was < 1%; entries 5–8: other by-products were ≤5% [total amount referred to the main product, PhCH(R)CN]. [c] Liquid-liquid phase-transfer catalysis (LL-PTC) conditions were used: 50% aq. KOH (11.5 cm^3/g substrate) and aliquat 336 (2% molar with respect to substrate).

solvent; entry 7, see Experimental section for details). In the case of $PhCH_2Cl$, the mono-benzylation selectivity was in the range 85–53% at conversions of 52–81%. There was no improvement with a decrease in the alkylating agent/substrate molar ratio (from 1.5 to 0.8) or a lowering of the reaction temperature. On the other hand, benzylation of phenylacetonitrile by $PhCH_2Cl$ under PTC conditions, was reported to be mono-benzyl selective only in the range 75–85% at conversions of 40–60%.[2e]

Table 3 reports the benzylation of different substrates by DBzlC in DMF and DEF solvents. At 155 °C, *O*-benzylation occurred more rapidly than *C*-benzylation. In particular, with a DBzlC/substrate of 1.1 the conversion of phenol was 93.5% after 2.0 h (entry 2) while, under the same reaction conditions, for phenylacetonitrile it was 90% after 6.0 h (entry 1).†

Benzyl phenyl acetate reacted more slowly than phenylacetonitrile (entry 3) and both a higher DBzlC/substrate molar ratio (1.5:1) and a higher reaction temperature (177 °C, refluxing DEF) were necessary to ensure comparable reaction times; thus, a conversion of 92% was reached after 4.5 h (entry 5). Similar behaviour was also observed in the methylation of arylacetic esters by DMC:[6c] methyl arylacetates required both higher reaction times and temperatures (≥220 °C) with respect to arylacetonitriles, to give the corresponding mono-methyl derivatives.

† Comparison of entry 2 of Table 1 and entry 1 of Table 3, suggests that the difference in the reaction times for the benzylation of $PhCH_2CN$ (4 and 6 h, respectively) is probably due to the very different amounts of the reacting substrates (0.5 g and 2.5 g, respectively). The results given in Table 3 allow a fairer comparison since comparable quantities of reagents are considered.

Discussion

At high temperatures (140–180 °C), DBzlC has proved to be an efficient benzylating agent of phenol and CH_2 acidic compounds, behaviour in which it strongly resembles DMC; nevertheless, methylation by DMC (occurring at 170–220 °C) necessarily requires an autoclave system while the higher boiling point of DBzlC allows benzylation to occur at atmospheric pressure. Since a solvent is used DBzlC can be employed in only a slight excess with respect to the reagent substrate; the best solvents have proved to be DMF and DEF (Tables 1–3).

Although the use of K_2CO_3 and DMF, in the alkylation of methylene-active compounds, is well established[9a,b] selective mono-alkylation with reactive alkyl halides under such conditions has been elusive. Thus, in DMF–KOH significant amounts (26%) of dialkyl derivative were obtained in the

Table 3 Benzylation of different substrates by dibenzyl carbonate

Entry*	Substrate	Solvent	Reaction time (t/h)	Temp. (T/°C)	Molar ratio (Sub/DBzlC)	Convn.[a] (%)	Product (R = CH_2Ph)	Yield[b] (%)
1	$PhCH_2CN$	DMF	6.0	155	1:1.1	90.0	PhCH(R)CN	82.0[c]
2	PhOH	DMF	2.0	155	1:1.1	93.5	PhOR[d]	80.0[e]
3	$PhCH_2CO_2CH_2Ph$	DMF	11.0	155	1:1.1	58.8	$PhCH(R)CO_2CH_2Ph$	
4	$PhCH_2CO_2CH_2Ph$	DEF	5.0	177	1:1.3	87.6	$PhCH(R)CO_2CH_2Ph$[d]	
5	$PhCH_2CO_2CH_2Ph$	DEF	4.5	177	1:1.5	92.1	$PhCH(R)CO_2CH_2Ph$[d]	83.0[c]

* 2 mol equiv. of K_2CO_3 were used in all reactions. [a] Determined by GC. [b] Yields based on isolated products. [c] Starting from 2.5 g of substrate. [d] Other by-products were ≤4% (entry 2) and ≤6% (entry 5): total amount is referred to PhOR and $PhCH(R)CO_2CH_2Ph$, respectively. [e] Starting from 2.0 g of substrate.

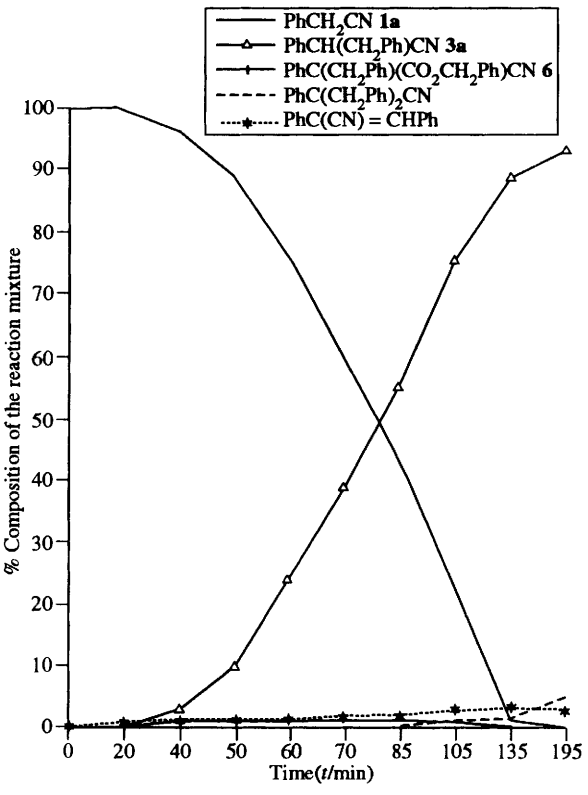


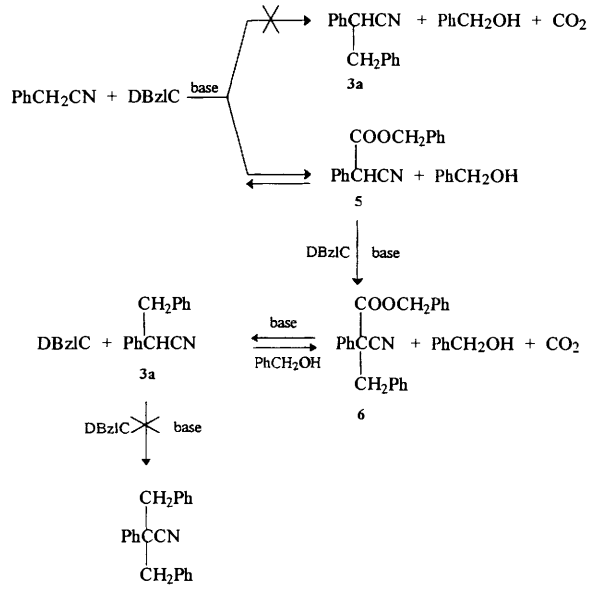
Fig. 1 The reaction of phenylacetonitrile with dibenzyl carbonate in DMF

benzylation of phenylacetonitrile by benzyl chloride.[10] In contrast, we obtained a high degree of mono-benzylation selectivity by use of DBzlC. Probably this reaction proceeds according to the mechanism already described for DMC,[6a-c] since in the benzylation of phenylacetonitrile by DbzlC an intermediate, 2-benzyl-2-carboxybenzylphenylacetonitrile, was shown to be present (by GC/MS).

Fig. 1 illustrates the course and Scheme 1 the proposed mechanism for a reaction employing $PhCH_2CN$, DBzlC and K_2CO_3 (1:1.5:2 mol ratio) in refluxing DMF.

Although the concentration of the intermediate **5** was too low for it to be detected, its formation is proposed on the basis that in the reaction of arylacetonitriles with DMC similar behaviour was noted. In fact, the corresponding carboxymethyl intermediates $ArCH(CO_2Me)CN$ were observed only during the methylation of *o*-tolyacetonitrile and *m*-carboxymethylphenylacetonitrile by DMC.[6c]

Since the carboxybenzyl group of the intermediate **5** has a protective function whilst at the same time increasing the acidity of the remaining hydrogen over that in the starting $PhCH_2CN$, subsequent benzylation gives the observed intermediate **6**. Finally, the decarboxybenzylation of **6** gives the



Scheme 1

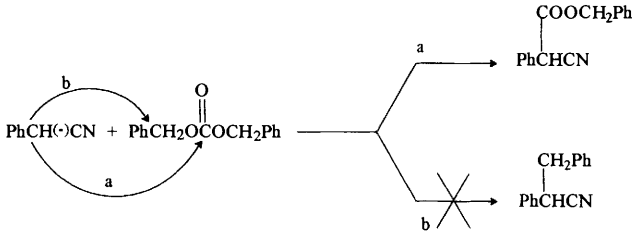


Fig. 2(*a*) $B_{Ac}2$ mechanism (path a). $B_{Al}2$ mechanism (path b)

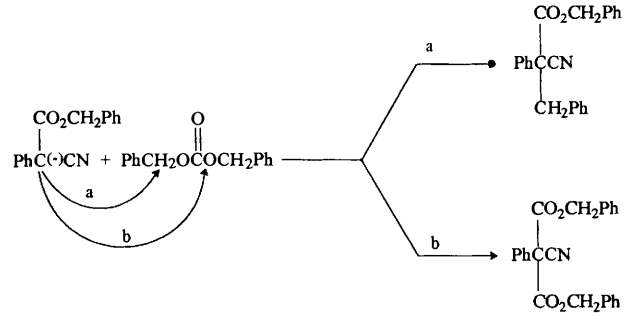


Fig. 2(*b*)

mono-benzyl derivative **3a**. Selectivity in the overall reaction may be explained in terms of attack by the anion $Ph(CN)CH^-$

on the acyl carbon of DBzlC (*via* a $B_{Ac}2$ mechanism) and not the benzyl carbon [Fig. 2(*a*)].

Instead, the second possible anionic species, $PhC^-(CO_2CH_2Ph)CN$ attacks both the alkyl (*via* a $B_{Al}2$ mechanism) and the acyl carbon of DBzlC; however, being an equilibrium reaction, the attack to the acyl carbon to produce the likely intermediate $PhC(CO_2CH_2)_2CN$ cannot effect the selectivity [Fig. 2(*b*)].

The driving force for the mono-benzylation is the non-equilibrium reaction following the $B_{Al}2$ mechanism [path (a) in Fig. 2(*b*)].

As in the alkylation by DMC, DBzlC does not produce an inorganic salt (as alkyl halides do) and the base can be used in catalytic amounts; these features make such alkylations of interest from an environmental point of view.

Conclusion

DBzlC seems to be particularly attractive as a selective benzylating agent since the reaction conditions are simple and the selectivity high (at almost complete conversion); the latter makes for easy separation of the mono-*C*-alkyl derivative from the reaction mixture.

At present, the reasons for such selectivity are not well understood; in particular, the reason why benzylation with DBzlC occurs only *via* the carboxybenzyl intermediate (**5** in Scheme I) with no direct benzylation. The softness and the hardness of the involved anions and the acid–base equilibria in Scheme 1, are likely to influence the reaction. Further applications of DBzlC are being studied.

Experimental

General

All compounds were ACS grade and were employed without further purification. Melting points were determined on a Buchi 535 melting-point apparatus and are uncorrected. ^1H NMR spectra were recorded on Varian Unity 400 (400 MHz) spectrometers using $CDCl_3$ with TMS as the internal standard. *J* Values are recorded in Hz. GC analyses were performed on a Varian GC 3300 using a fused silica capillary column (30 m × 0.25 mm) with DB5 as liquid phase (film thickness 0.25 mm). GC/MS analyses were performed on a HP 5971 mass detector coupled to a HP 5890 gas chromatograph fitted with a 30 m × 0.25 mm, DB5 capillary column.

Dibenzyl carbonate 7

A stirred mixture of benzyl alcohol (20.0 g, 0.18 mol), dimethyl carbonate (46.7 cm^3, 0.55 mol) and K_2CO_3 (25.6 g, 0.18 mol) was heated at 85 °C, in a round-bottomed flask fitted with a Liebig condenser for 24 h, after which the excess of dimethyl carbonate was removed by distillation under reduced pressure. Benzyl alcohol (20.0 g, 0.18 mol) was added to the residue and the mixture heated to 120 °C; the reaction was performed under reduced pressure (20 mmHg), in order to ensure removal of methanol. After 6 h, the mixture was cooled to room temperature and the K_2CO_3 filtered off and washed with diethyl ether (100 cm^3). The combined filtrate and washings were concentrated after which the excess of benzyl alcohol was removed by distillation under reduced pressure to give the title compound **7** (27.7 g, 62%) as a pale yellow liquid [11a–e] (95.6% by GC) which, with time, slowly crystallized. It was recrystallized from pentane to give a white solid, mp 27.3–29.1 °C (lit.,[11e] bp 197–198 °C/12 mmHg); δ_H 5.17 (s, 4 H, $2CH_2$) and 7.32–7.38 (m, 10 H, 2 Ph).

Benzyl phenylacetate 8

A mixture of phenylacetic acid (10.0 g, 73 mmol), benzyl alcohol (20.0 g, 180 mmol) and toluene-*p*-sulfonic acid monohydrate (1.8 g, 9.1 mmol) was set aside at room temperature for 15 h after which a solution of $KHCO_3$ (2.5 g, 29 mmol) in water (20 cm^3) was added to it with stirring. The mixture was extracted with diethyl ether (3 × 30 cm^3) and the combined extracts were dried (Na_2SO_4) and distilled through a Vigreux column to afford the title compound **8** (12.6 g, 76%), bp 106–109 °C/0.07 mmHg (purity > 99% by GC lit.,[12] bp 137–140 °C/1.5 mmHg); δ_H 3.65 (s, 2 H, CH_2), 5.12 (s, 2 H, CH_2) and 7.28–7.31 (m, 10 H, 2 Ph); *m/z* 226 (M^+, 10%), 92 (17), 91 (100), 77 (6), 65 (28) and 51 (8).

Benzylations: general procedure

The reactions were carried out by charging a 3-necked, round-bottomed flask, equipped with a condenser, a stop-cock and a glass screw-capped tube (fitted with a rubber silicon septum) used for sample withdrawal, with the substrate, DBzlC (or $PhCH_2Cl$) (1.1–3.0 mol equiv. with respect to the substrate, see Tables 1–3), K_2CO_3 (2 mol equiv. with respect to the substrate) and solvent (~ 12 cm^3 g^{-1} substrate; see Table 1 for details). The flask was flushed both before and during the reaction with nitrogen. The reaction mixtures, magnetically stirred and heated in an oil-bath to the appropriate temperature, were analysed by GC.

In order both to facilitate the separation of the products **3a** and **9** and to evaluate their yields, the slight excess of DBzlC present at the end of the reaction was hydrolysed at room temperature, with 5% aq. NaOH.

Benzyl phenyl ether 9

A mixture of phenol (2.0 g, 22 mmol), DBzlC (5.7 g, 23 mmol), K_2CO_3 (5.9 g, 42 mmol) and DMF (25 cm^3) was heated for 2 h under reflux (~ 155 °C), as described above. After the mixture had been cooled to room temperature it was treated with 5% aq. NaOH (5 cm^3), stirred for 30 min, diluted with water (100 cm^3) and extracted with diethyl ether (3 × 40 cm^3). The combined extracts were dried (Na_2SO_4) after which the benzyl alcohol present was removed by distillation under reduced pressure to leave the title compound **9** (3.1 g, 79.5%) as a liquid (purity 92% by GC) which rapidly crystallized. It was recrystallized from pentane to give white needles, mp 38.4–39.0 (lit.,[13a] mp 40 °C); δ_H 5.06 (s, 2 H, CH_2) and 6.96–7.45 (m, 10 H, 2 Ph).

2,3-Diphenylpropionitrile 3a

A mixture of $PhCH_2CN$ (2.5 g, 21 mmol), DBzlC (5.7 g, 23 mmol), K_2CO_3 (5.9 g, 42 mmol) and DMF (30 cm^3) was heated for 6 h under reflux (~ 155 °C) as described above. After the mixture had been allowed to cool to room temperature, it was treated with 5% aq. NaOH (15 cm^3), stirred for 20 min, diluted with water (100 cm^3) and extracted with diethyl ether (3 × 35 cm^3). The combined extracts were dried (Na_2SO_4) and the benzyl alcohol present was removed by distillation under reduced pressure to leave compound **3a** (3.6 g, 82%) as a pale yellow liquid (purity 91.5% by GC) that crystallized with time. The product was recrystallized from $CHCl_3$–hexane to give a white solid, mp 55.6–56.2 (lit.,[13b] mp 58 °C); δ_H 3.16 (dq, 2 H, $J_{2,2'}$ 21.4, $J_{1,2}$ = 8.0, $J_{1,2'}$ = 6.6, CH_2), 3.99 (dd, 1 H, CH) and 7.13–7.38 (m, 10 H, 2 Ph); *m/z* 207 (M^+, 18%), 116 (3), 92 (7), 91 (100), 65 (14) and 51 (5).

Benzyl 2,3-diphenylpropionate 3b

A mixture of $PhCH_2CO_2CH_2Ph$ (2.5 g, 11 mmol), DBzlC (4.0 g, 16 mmol), K_2CO_3 (3.1 g, 22 mmol) and *N*,*N*-diethylformamide (30 cm^3) was heated under reflux (~ 177 °C) for 4.5 h as described above and then allowed to cool to room temperature. The K_2CO_3 was filtered off and the benzyl alcohol present together with the residual reagents were distilled from the reaction mixture under reduced pressure. The residue was purified by gravity column chromatography (gradient elution)

using light petroleum–diethyl ether (95:5, v/v) as eluent to give the title compound **3b** (2.9 g, 83%) as a pale yellow liquid [14a–c] (purity 97.5% by GC); δ_H 3.15 and 3.44 (dd, 2-H, $J_{2,2'}$ 13.9, $J_{1,2}$ 9.2, $J_{1,2'}$ 6.4, CH_2), 3.93 (dd, 1-H, CH), 4.99 and 5.09 (dd's, 3-H, $J_{3,3'}$ 12.5, CH_2) and 7.09–7.34 (m, 15 H, 3 Ph); *m/z* 316 (M^+, 1%), 225 (6), 181 (100), 166 (17), 165 (18), 91 (94), 77 (14) and 65 (14) (Found: C, 84.1; H, 6.35. Calc. for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37%).

Benzylation of phenylacetonitrile under PTC conditions

Two procedures were used.

(a) Liquid-liquid phase-transfer catalysis (LL-PTC; entries 7–8, Table 2).[15] A mixture of $PhCH_2CN$ (0.70 g, 5.98 mmol), $PhCH_2Cl$ (0.75 g, 5.92 mmol) and aliquat 336 (0.048 g, ≅0.12 mmol) dissolved in toluene (8 cm^3) together with aqueous KOH (50%; 8 cm^3) was stirred at room temperature with monitoring of the reaction by GC.

(b) Solid-liquid phase-transfer catalysis (SL-PTC; entries 7, Table 1).[15] Three separate mixtures of $PhCH_2CN$ (0.50 g, 4.27 mmol), DBzlC (1.14 g, 4.71 mmol) and aliquat 336 (0.034 g, ≅0.084 mmol) dissolved in xylene (6 cm^3) together with K_2CO_3 (1.18 g, 8.53 mmol) were stirred at 90, 110 and 140 °C, respectively with monitoring of each reaction by GC.

Acknowledgements

This work was supported by Tessenderlo Chemie, (Belgium): It. Pat. Appl. MI94AN00020 (04/02/1994). Dr A. Bomben is gratefully acknowledged for his help in the synthesis of dibenzyl carbonate.

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Paper 5/01365H
Received 6*th March* 1995
Accepted 18*th April* 1995