

Table 1 Benzoylation 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 ₂ Ph)	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
		6.0	180	1:1.1	62.2	100	60.0	—	2.2
3	Triglyme	2.0	160	1:1.1	8.0	—	—	—	—
		8.25	180	1:3.0	93.1	99.5	90.8	0.5	1.8
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 K₂CO₃ were used in all reactions. ^b PhCH₂CN/DBzlC molar ratio. ^c Selectivity is defined as: $[\text{PhCH(R)CN}]/\{[\text{PhCH(R)CN}] + [\text{PhC(R}_2\text{)CN}]\} \times 100$; R = CH₂Ph. ^d Other by-products were PhCH₂OCH₂Ph, PhCOOCH₂Ph, PhCH₂COPh 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 Benzoylation 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 ₂ Ph)	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
		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 ₂ Cl	1:0.8	48.1	84.9	40.6	7.2	0.3
6	DMF	4.0	80	PhCH ₂ Cl	1:1.5	82.3	64.9	52.1	28.2	2.0
7	Toluene ^c	4.0	rt	PhCH ₂ Cl	1:1	18.2	93.4	17.0	1.2	—
		19.5	rt	PhCH ₂ Cl	1:1	81.1	53.1	41.1	36.3	3.7

* Entries 1–6: 2 mol equiv. of K₂CO₃ were used. ^a The selectivity is defined as: $[\text{PhCH(R)CN}]/\{[\text{PhCH(R)CN}] + [\text{PhC(R}_2\text{)CN}]\} \times 100$; R = CH₂Ph. ^b Entries 1–4: other by-products were PhCH₂OCH₂Ph, PhCOOCH₂Ph, PhCH₂COPh 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 cm³/g substrate) and aliquat 336 (2% molar with respect to substrate).

solvent; entry 7, see Experimental section for details). In the case of PhCH₂Cl, the mono-benzoylation 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, benzoylation of phenylacetonitrile by PhCH₂Cl 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 benzoylation of different substrates by DBzlC in DMF and DEF solvents. At 155 °C, *O*-benzoylation occurred more rapidly than *C*-benzoylation. 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.

Discussion

At high temperatures (140–180 °C), DBzlC has proved to be an efficient benzoylating agent of phenol and CH₂ 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 benzoylation 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).

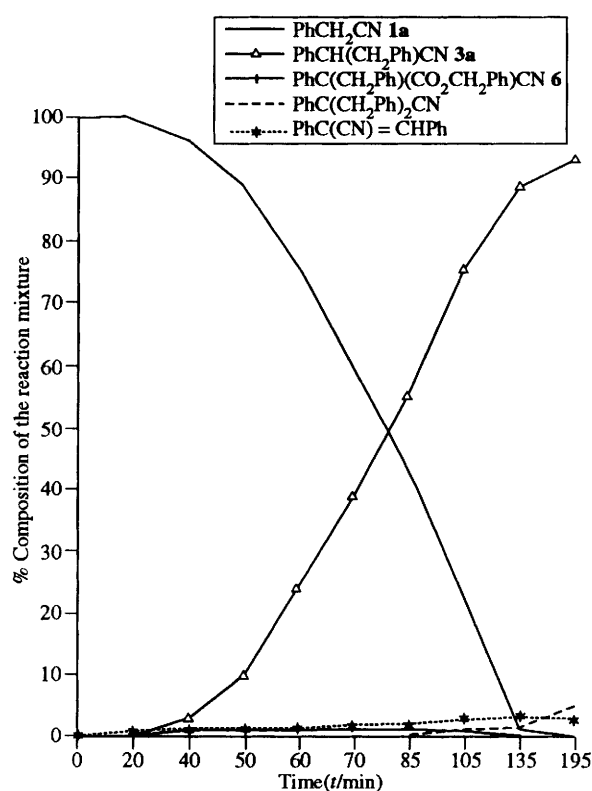
Although the use of K₂CO₃ and DMF, in the alkylation of methylene-active compounds, is well established^{9a,b} selective mono-alkylation with reactive alkyl halides under such conditions has been elusive. Thus, in DMF–KOH significant amounts (26%) of dialkyl derivative were obtained in the

† Comparison of entry 2 of Table 1 and entry 1 of Table 3, suggests that the difference in the reaction times for the benzoylation of PhCH₂CN (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.

Table 3 Benzoylation of different substrates by dibenzyl carbonate

Entry*	Substrate	Solvent	Reaction time (t/h)	Temp. (T/°C)	Molar ratio (Sub/DBzIC)	Convsn. ^a (%)	Product (R = CH ₂ Ph)	Yield ^b (%)
1	PhCH ₂ CN	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 ₂ CO ₂ CH ₂ Ph	DMF	11.0	155	1:1.1	58.8	PhCH(R)CO ₂ CH ₂ Ph	
4	PhCH ₂ CO ₂ CH ₂ Ph	DEF	5.0	177	1:1.3	87.6	PhCH(R)CO ₂ CH ₂ Ph ^d	
5	PhCH ₂ CO ₂ CH ₂ Ph	DEF	4.5	177	1:1.5	92.1	PhCH(R)CO ₂ CH ₂ Ph ^d	83.0 ^c

* 2 mol equiv. of K₂CO₃ 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)CO₂CH₂Ph, respectively. ^e Starting from 2.0 g of substrate.

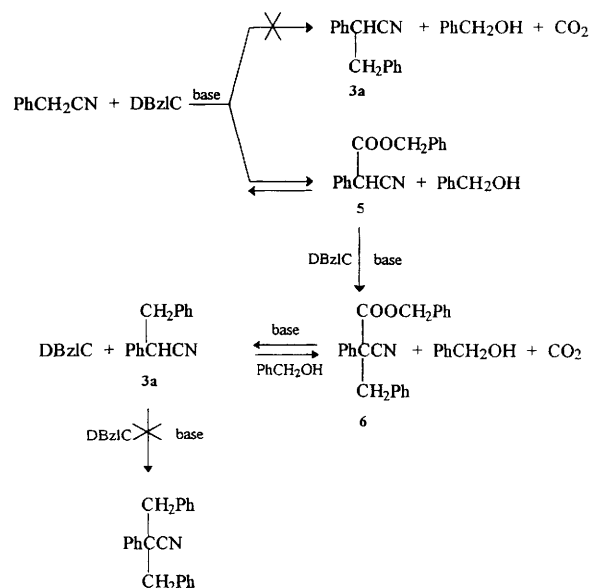
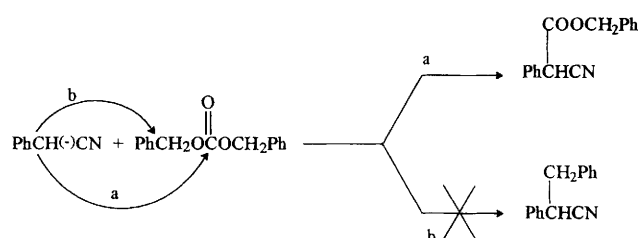
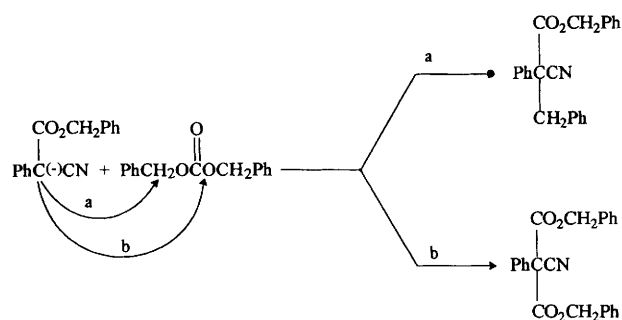
**Fig. 1** The reaction of phenylacetone nitrile with dibenzyl carbonate in DMF

benzoylation of phenylacetone nitrile by benzyl chloride.¹⁰ In contrast, we obtained a high degree of mono-benzoylation selectivity by use of DBzIC. Probably this reaction proceeds according to the mechanism already described for DMC,^{6a-c} since in the benzoylation of phenylacetone nitrile by DbzIC an intermediate, 2-benzyl-2-carboxybenzylphenylacetone nitrile, was shown to be present (by GC/MS).

Fig. 1 illustrates the course and Scheme 1 the proposed mechanism for a reaction employing PhCH₂CN, DBzIC and K₂CO₃ (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 arylacetone nitriles with DMC similar behaviour was noted. In fact, the corresponding carboxymethyl intermediates ArCH(CO₂Me)CN were observed only during the methylation of *o*-tolylacetone nitrile and *m*-carboxymethylphenylacetone nitrile 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 PhCH₂CN, subsequent benzoylation gives the observed intermediate **6**. Finally, the decarboxybenzoylation of **6** gives the

**Scheme 1****Fig. 2(a)** B_{Ac}2 mechanism (path a). B_{A2} 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 DBzIC (*via* a $B_{Ac}2$ mechanism) and not the benzyl carbon [Fig. 2(a)].

Instead, the second possible anionic species, $PhC^-(CO_2CH_2-Ph)CN$ attacks both the alkyl (*via* a $B_{Al}2$ mechanism) and the acyl carbon of DBzIC; 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-benylation is the non-equilibrium reaction following the $B_{Al}2$ mechanism [path (a) in Fig. 2(b)].

As in the alkylation by DMC, DBzIC 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

DBzIC 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 DBzIC occurs only *via* the carboxybenzyl intermediate (5 in Scheme 1) 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 DBzIC 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 \times 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 \times 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 cm³, 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 cm³). 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, 2CH₂) 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 cm³) was added to it with stirring. The mixture was extracted with diethyl ether (3 \times 30 cm³) 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, CH₂), 5.12 (s, 2 H, CH₂) 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).

Benzylation: 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, DBzIC (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 cm³ 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 DBzIC 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), DBzIC (5.7 g, 23 mmol), K_2CO_3 (5.9 g, 42 mmol) and DMF (25 cm³) 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 cm³), stirred for 30 min, diluted with water (100 cm³) and extracted with diethyl ether (3 \times 40 cm³). 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, CH₂) and 6.96–7.45 (m, 10 H, 2 Ph).

2,3-Diphenylpropionitrile 3a

A mixture of $PhCH_2CN$ (2.5 g, 21 mmol), DBzIC (5.7 g, 23 mmol), K_2CO_3 (5.9 g, 42 mmol) and DMF (30 cm³) 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 cm³), stirred for 20 min, diluted with water (100 cm³) and extracted with diethyl ether (3 \times 35 cm³). 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, $J_{2,2'} 21.4$, $J_{1,2} = 8.0$, $J_{1,2'} = 6.6$, CH₂), 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), DBzIC (4.0 g, 16 mmol), K_2CO_3 (3.1 g, 22 mmol) and *N,N*-diethylformamide (30 cm³) 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, CH₂), 3.93 (dd, 1-H, CH), 4.99 and 5.09 (dd's, 3-H, $J_{3,3}$: 12.5, CH₂) 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 C₂₂H₂₀O₂: 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 PhCH₂CN (0.70 g, 5.98 mmol), PhCH₂Cl (0.75 g, 5.92 mmol) and aliquat 336 (0.048 g, \cong 0.12 mmol) dissolved in toluene (8 cm³) together with aqueous KOH (50%; 8 cm³) 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 PhCH₂CN (0.50 g, 4.27 mmol), DBzIc (1.14 g, 4.71 mmol) and aliquat 336 (0.034 g, \cong 0.084 mmol) dissolved in xylene (6 cm³) together with K₂CO₃ (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.

References

- (a) A. C. Cope, H. L. Holmes and H. O. House, *Org. React.*, 1957, **9**, 107; (b) W. C. Kenyon, E. M. Kaiser and C. H. Hauser, *J. Org. Chem.*, 1965, **30**, 2937; (c) W. C. Kenyon, E. M. Kaiser and C. H. Hauser, *J. Org. Chem.*, 1965, **30**, 4135; (d) M. W. Rathke and A. Lindert, *J. Am. Chem. Soc.*, 1971, **93**, 2318; (e) D. S. Watt, *Tetrahedron Lett.*, 1974, 707; (f) D. Savoia, C. Trombini and A. Umani-Ronchi, *Tetrahedron Lett.*, 1977, 653; (g) A. A. Gevorkyan, P. I. Kazaryan, S. V. Avakyan and Yu. M. Blazhin, *Oktryitiya, Izobret., Prom. Obratzy, Tovarnye Znaki*, 1982, **30**, 88 (*Chem. Abstr.*, 1983, **98**, 53186v), (h) X. Peng, and C. Xu, *Huaxue Xubao*, 1983, **41**, 514 (*Chem. Abstr.*, 1983, **99**, 121779p); (i) K. Sukata, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3306; (j) S. Arseniyadis, K. S. Kyler and D. S. Watt, *Org. React.*, 1984, **31**, 1; (k) J. P. Rieu, A. Boucherle, H. Cousse and G. Mouzin, *Tetrahedron*, 1986, **42**, 4095; (l) A. A. Vasil'eval, V. A. Petrosyan, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1991, **9**, 2160. (*Chem. Abstr.*, 1992, **116**, 20750f).
- (a) M. Makosza, *Tetrahedron*, 1968, **24**, 175; (b) A. Branstrom and U. Junggren, *Tetrahedron Lett.*, 1972, 472; (c) C. M. Starks and C. Liotta, *Phase-Transfer Catalysis, Principles and Techniques*, Academic Press, New York, 1976; ch. 5, p. 170; (d) W. P. Weber and G. W. Gokel, *Phase-Transfer Catalysis in Organic Chemistry*, Springer Verlag, West Berlin, 1977; (e) E. V. Dehmlov and S. S. Dehmlov, *Phase-Transfer Catalysis*, Verlag Chemie, Weinheim, 1983, ch. 3, p. 123.
- (a) E. M. Kaiser and C. H. Hauser, *J. Org. Chem.*, 1966, **31**, 3873; (b) S. Miyano and N. Abe, *Chem. Pharm. Bull.*, 1970, **18**, 550; (c) R. Grigg, T. R. B. Mitchell, S. Sutthivaiyakit and N. Tongpenyai, *Tetrahedron Lett.*, 1981, 4107; (d) T. Shono, S. Kashimura and H. Nogusa, *J. Org. Chem.*, 1984, **49**, 2043; (e) J. C. Folest, S. Guibe, J. Y. Nedelec and J. Perichon, *J. Chem. Res.*, 1990, (s), 258; (f) F. Abe, T. Hayashi and M. Tanaka, *Chem. Lett.*, 1990, 765; (g) M. Tanaka, T. Hayashi and F. Abe, JP 03,246,249, 01 Nov. 1991, Appl. 90/40,238 (*Chem. Abstr.*, 1992, **116**, 127822p); (h) M. Tanaka, H. Teruyuki, T. Norio, A. Kazutaka and T. Shinichiro JP 04,290,834, 15 Oct. 1992, Appl. 91/80,829 (*Chem. Abstr.*, 1993, **118**, 124185p).
- (a) P. Tundo, G. Moraglio and F. Trotta, *Ind. Eng. Chem. Res.*, 1989, **28**, 881; (b) P. Tundo, F. Trotta and G. Moraglio, *J. Chem. Soc., Perkin Trans. I*, 1989, 1070.
- P. Tundo, *Continuous Flow Methods In Organic Synthesis*, E. Horwood, Chichester, 1991.
- (a) P. Loosen, P. Tundo and M. Selva, It. Pat. Appl. MI92A00081; (b) P. Loosen, P. Tundo and M. Selva, US Pat. Appl. 922140; Jap. Pat Appl. 4-223302; (c) C. A. Marques, M. Selva and P. Tundo, *J. Chem. Soc., Perkin Trans. I*, 1994, 1323.
- P. Tundo, F. Trotta, G. Moraglio and F. Ligorati, *Ind. Eng. Chem. Res.*, 1988, **28**, 1565–71.
- (a) D. Lee and V. Chang, *J. Org. Chem.*, 1978, **43**, 1532; (b) M. Shirai and J. Smid, *J. Am. Chem. Soc.*, 1980, **102**, 2865; (c) J. M. Harris, N. H. Hudley, T. G. Shannon and E. C. Struck, *J. Am. Chem. Soc.*, 1982, **47**, 4789.
- (a) D. A. White, *Synth. Comm.*, 1977, **7**, 559; (b) N. N. Sukhanov, L. N. Trappel, V. P. Chetverkov and L. A. Yanovskaya, *Zh. Org. Khim.*, 1985, **21**, 2503 (*Chem. Abstr.*, 1986, **105**, 225743f).
- V. A. Volkova and D. V. Ioffe, *Zh. Org. Khim.*, 1972, **7**, 2177 (*Chem. Abstr.*, 1972, **76**, 14048c).
- (a) G. C. Overberger, L. C. Palmer, B. S. Marks and N. R. Byrd, *J. Am. Chem. Soc.*, 1955, **77**, 4100; (b) K. Kondo, N. Sonoda and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 108; (c) M. Lissel and E. V. Dehmlov, *Chem. Ber.*, 1981, **114**, 1210; (d) A.-A. G. Shaik and S. Sivaram, *Ind. Eng. Chem. Res.*, 1992, **31**, 1167; (e) T. Mizuno, F. Nakamura, Y. Egashira, I. Nishiguchi, T. Hirashima, A. Ogawa, N. Kambe and N. Sonoda, *Synthesis*, 1989, 636.
- S. Kim, J. I. Lee and Y. C. Kim, *J. Org. Chem.*, 1985, **50**, 560.
- (a) *Dictionary of Org. Compounds*, 5th edn., Chapman and Hall, New York, 1982, vol. 1, p. 626; (b) vol. 2, p. 2336.
- (a) L. I. Smith, *C. R. Seances Acad Sci*, 1924, **178**, 1583 (*Chem. Abstr.*, 1924, **18**, 2881²); (b) J. H. Billman and J. L. Rendall, *J. Am. Chem. Soc.*, 1944, **66**, 745; (c) R. A. Zingaro, *Ethyl Corp.* BP. 872,757 Appl. Oct. 30. 1957 (*Chem. Abstr.*, 1962, **56**, 7222p).
- F. Montanari, D. Landini and F. Rolla, *Top. Curr. Chem.*, 1982, **101**, 147.

Paper 5/01365H

Received 6th March 1995

Accepted 18th April 1995