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1,5-BIS-(N-BENZYL-N,N-DIETHYLAMMONIUM) DIETHYLETHER, DICHLORIDE (BBDE Cl)[#]. A NOVEL BIS-AMMONIUM SALT AS PHASE TRANSFER CATALYST.

Julio Alvarez-Builla[a]*, Juan J. Vaquero[a], Jose L. Garcia Navio[a], Juan F. Cabello[a], Carlos Sunkel[b], Miguel Fau de Casa-Juana[b], Fernando Dorrego[b] and Luis Santos[b].

[a] Departamento de Química Orgánica. Universidad de Alcalá de Henares. Madrid. Spain.

[b] Departamento de Investigación. ALTER S. A.. Mateo Inurria 30. 28036 Madrid. Spain.

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Abstract: 1,5-Bis-(N-benzyl-N,N-diethylammonium)diethyl ether, dichloride (BBDE Cl) has been tested as phase transfer catalyst. Several test reactions have been performed, comparing yields obtained with several commercial catalysts, involving the transference of different nucleophiles. Williamson reactions on diphenols were used to test its ability in transferring dinucleophiles, producing higher yields at lower concentrations.

Phase Transfer Catalysis (PTC)[1,2] has become in recent years one of the most widely used techniques in organic synthesis, advantageously applied to a great number of organic transformations. As an index of the generated interest on the method, several reviews[3-8], monographs[9-12] and even an ACS Audio Course[13] have recently appeared, describing the phase transfer process and providing compilations of catalysts, techniques and reaction types.

Two groups of catalysts have been used in the technique, the first one being the so called "crown ethers" group, including not only them but also open chain poliethylenglycol ethers, cryptands etc., usually non charged products with long chains, bearing heteroatoms at regular distances, which can chelate inorganic cations converting them into lipophilic cationic species. The other group is the so called "quats" formed by either quaternary ammonium or phosphonium salts, usually able of generating lipophilic ion pairs with anionic species.

[#]Systematic name: 1,5-bis(N-benzyl-N,N-diethylammonio)-3-oxapentane dichloride

From the many ideas proposed for the development of new and more efficient "quat" catalysts, there has been several reports describing "multi-site" catalysts[14,15], normally polymer supported, emphasizing the interest of catalysts bearing more than one quaternary group per molecule, allowing to use smaller concentrations to achieve the same yield.

A recent publication from Brunelle[16] emphasized the interest of bis-quaternary salts with appropriate spacing between the quaternary nitrogens, to improve transfer of divalent anions (Fig. 1), in addition with its efficiency at low concentrations. Both charactheristics are of great interest in the industrial field.

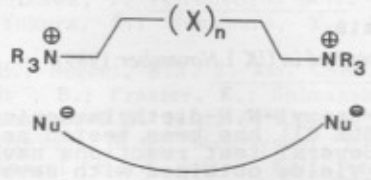


Fig 1

Simultaneously to the publication from Brunelle, we were trying to find the way of using bis-dialkylaminoethyl ethers 4 (Fig 2) formed as subproducts in synthesis of pharmaceuticals involving the alkylation of a nucleophile with a dialkylaminoethyl chloride, in the presence of base. Quaternisation of those amino ethers produced a series of bis-quaternary salts 5 (Fig. 2), which have been already described in different patents[17,18].

We report here results concerning the preparation and uses as phase transfer catalyst of 1,5-bis-(N-benzyl-N,N-diethylammonium)diethylether dichloride (BBDE Cl) (5, R^1, R^2 = Et; R^3 = Bz; X = Cl) which presented the best efficiency/price/toxicity compromise.

The product was obtained by a Williamson synthesis as shown in Fig. 2, and the diamine was quaternised with benzyl chloride. Subsequently, a battery of different PTC-reactions were performed with the selected catalyst. So, classical alkylation reactions with different nucleophiles (Table 1), additions on sp^2 carbon substrates (Table 1) and redox processes (Table 2) were tested in comparison with described catalysts to asses the behaviour of BBDE Cl. The catalysts used as controls include those "quats" which have been the most extensively used and were commercially available: Tetrabutylammonium Bromide (TBAB), Tetrabutylammonium Hydrogensulphate (TBAS) and

Triethylbenzylammonium Chloride (TEBA Cl). All processes were performed as described in cited references, usually as liquid-liquid systems, using 50% aqueous NaOH and benzene or toluene as organic phase. However, some of them worked better when no organic solvent was used, or even with a solid-liquid system.

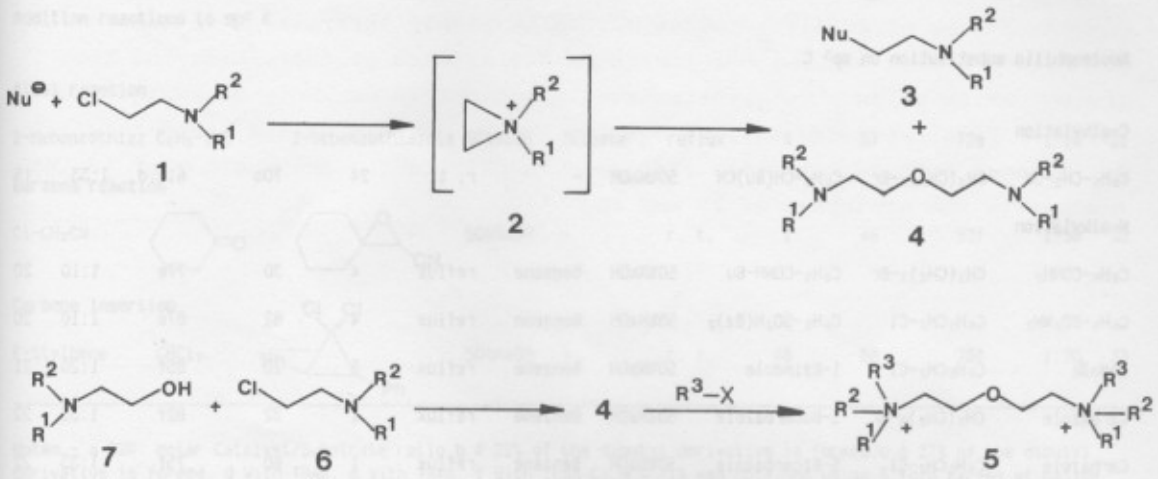
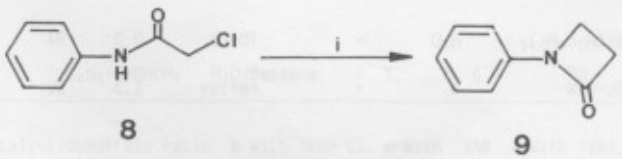


Fig 2

As it can be seen in Table 1, alkylation of phenylacetonitrile, and carbazole was achieved with comparatively high yields, as well as ether synthesis, oxime alkylation and sulphide and thiocyanate preparation. In the redox processes (Table 2), transference of potassium permanganate was highly effective.

Other experiments not included in Tables 1 and 2 involved the synthesis of 1-phenyl-2-azetidinone 9 by intramolecular alkylation of an amide, as described by Takahata and coworkers[35], shown in Fig. 3.



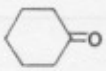
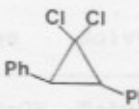
BBDE Cl 69%
TBAB 89%

Fig. 3 i: KOH, CH_2Cl_2, r. t., 6 h, CSR 1:10

Table 1. Test reactions with electrophiles.

Substrate	Electrophile	Product	Base	Solvent	Temp.(°C)	Time(h)	Yield % BBDE Cl	Yield % TestCat.	CSR	Ref
Nucleophilic substitution on sp^3 C										
C-alkylation										
C_6H_5-CH_2-CN	$CH_3(CH_2)_3$-Br	C_6H_5-CH(Bu)CN	50%NaOH	-	r. t.	24	70b	61c,d	1:33	19
N-alkylation										
C_6H_5-$CONH_2$	$CH_3(CH_2)_3$-Br	C_6H_5-CONH-Bu	50%NaOH	Benzene	reflux	4	30	77e	1:10	20
C_6H_5-SO_2NH_2	$C_6H_5CH_2$-Cl	C_6H_5-$SO_2N(Bz)_2$	50%NaOH	Benzene	reflux	4	82	87e	1:10	20
Indole	$C_6H_5CH_2$-Cl	1-Bzindole	50%NaOH	Benzene	reflux	5	70	85f	1:20	21
Carbazole	$CH_3(CH_2)_3$-Br	5-Bucarbazole	50%NaOH	Benzene	reflux	1	82	82f	1:33	22
Carbazole	$C_6H_5CH_2$-Cl	5-Bzcarbazole	50%NaOH	Benzene	reflux	1	80	75f	1:33	22
Imidazole	$C_6H_5CH_2$-Cl	1-Bzimidazole	KOH/K_2CO_3	MeCN	r. t.	20	73	53e,h	1:20	23
2-Mebenzimidaz.	$CH_3(CH_2)_3$-Br	1-Bu-2-Mebenzim.	50%NaOH	Toluene	80-85	3	65	91d	1:25	24
O-alkylation										
Phenol	$(CH_3O)_2SO_2$	MeO-benzene	50%NaOH	CH_2Cl_2	r. t.	10	65	79d	1:20	25
Phenol	$(CH_3O)_2SO_2$	MeO-benzene	50%NaOH	Benzene	reflux	5	65	66d	1:20	25
Phenol	$BrCH_2COOEt$	C_6H_5O-CH_2COOEt	50%NaOH	CH_2Cl_2	r. t.	10	40	72d	1:20	25
n-Butanol	$C_6H_5CH_2$-Cl	n-BuO-Bz	50%NaOH	-	50-60	4	90	76d	1:20	26
$(C_6H_5)_2C$=NOH	$C_6H_5CH_2$-Cl	$(C_6H_5)_2C$=NOBz	50%NaOH	Benzene	reflux	4	90	87d	1:20	27
C_6H_5-COOH	$C_6H_5CH_2$-Cl	C_6H_5COOBz	K_2CO_3	CH_2Cl_2	reflux	10	62g	62e	1:25	28
S-alkylation										
Na_2S	$C_6H_5CH_2$-Cl	$S(CH_2C_6H_5)_2$	H_2O	-	70-75	0.3	94	94d	1:20	29
KSCN	$CH_3(CH_2)_3$-Br	Bu-SCN	-	-	reflux	1.3	80	84d	1:20	30

Table 1 (Cont). Test reactions with electrophiles.

Substrate	Electrophile	Product	Base	Solvent	Temp.(°C)	Time(h)	Yield % BBDE Cl	Yield % TestCat.	CSR	Ref
Addition reactions to sp^2 C										
Aldol reaction										
2-Mebenzothiaz	C_6H_5-CHO	2-Stbenzothiazole	50%NaOH	Toluene	reflux	4	57	72e	1:10	31
Darzens reaction										
Cl-CH_2CN			50%NaOH	-	r. t.	1	46	52f	1:50	32
Carbene insertion										
E-Stylbene	$CHCl_3$		50%NaOH	-	r. t.	48	58	75f	1:20	33

Notes.- a CSR: Molar Catalyst/Substrate ratio.b A 22% of the dibutyl derivative is formed.c A 27% of the dibutyl derivative is formed. d With TBAB. e With TBAS. f With TEBA Cl.g A 71% was obtained using 5 fold excess of halide. h The original process was modified, using acetonitrile at room temperature instead of refluxing xylene.

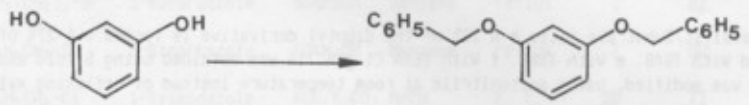
Abbreviations.- Bu:Butyl; Bz:Benzyl; Me:Methyl; St:Styryl.

Table 2. Redox processes.

Substrate	Redox Agent	Product	Solvent	Temp.(°C)	Time (h)	Yield % BBDE Cl	Yield % Test Cat.	CSR	Ref
Oxidation									
$C_6H_5CH_2$-OH	$KMnO_4$	C_6H_5-COOH	H_2O/Benzene	r. t.	3	75	76b	1:20	34
$C_6H_5CH_2$-CN	$KMnO_4$	C_6H_5-COOH	H_2O/Benzene	r. t.	3	63	60c	1:20	34
Reduction									
C_6H_5-$COCH_3$	$NaBH_4$	C_6H_5-$CHOHCH_3$	H_2O/Benzene	r. t.	6	70	90d	1:10	35

Notes.-a CSR:Molar Catalyst/Substrate ratio. b With TEBA Cl. c With TBAB. d With TBAS.

After the use of BBDE Cl as "single" catalyst, other experiments were planned to test its ability in transferring several dinucleophiles. Diphenols were the first selected substrates, and Williamson ether synthesis was performed on resorcinol **10**, phenolphthalein **12** and 2,2-bis-(4',4'-hydroxiphenyl)propane **14**, by treating them with alkyl halides, using either BBDE Cl or TBAB. As it can be seen in Table 3, using BBDE Cl allows the use of smaller concentrations of catalyst, which should be highly interesting in the industrial field, with higher yields in dialkylated product. Reducing the concentration below a catalyst:substrate ratio 1:40 markedly decreases the yield of final product. Similar results can be seen in Tables 4 and 5, with differences between catalysts efficiency higher in the preparation of **13** and smaller in the synthesis of **15** and **16**.

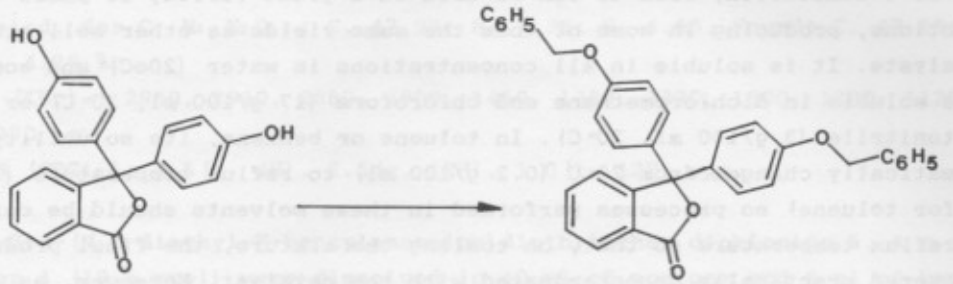


10 **11**

Table 3

RX	Base	Solvent	Temp (° C)	Time (h)	Yield % BBDE Cl	Yield % TBAB	CSR
$C_6H_5CH_2-Cl$	50% NaOH	---	80	15	56	38	1:20
$C_6H_5CH_2-Cl$	50% NaOH	---	80	15	57	37	1:40
$C_6H_5CH_2-Cl$	50% NaOH	---	80	15	19	15	1:50
$C_6H_5CH_2-Cl$	50% NaOH	Benzene	Reflux	5	52	--*	1:20

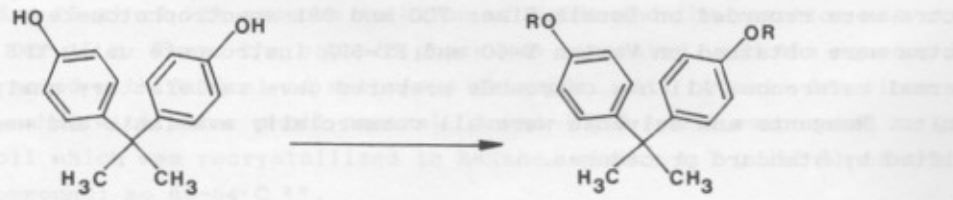
Notes.- * No experiment was performed.



12 13

Table 4

RX	Base	Solvent	Temp (° C)	Time (h)	Yield % BBDE Cl	Yield % TBAB	CSR
$C_6H_5CH_2-Cl$	50% NaOH	Toluene	Reflux	5	74	37	1:20
$C_6H_5CH_2-Cl$	50% NaOH	Toluene	Reflux	5	74	38	1:40



14

15 ; R=$CH_2C_6H_5$

16 ; R=CH_2CO_2Et

Table 5

RX	Base	Solvent	Temp (° C)	Time (h)	Yield % BBDE Cl	Yield % TBAB	CSR
$C_6H_5CH_2-Cl$	50% NaOH	Toluene	Reflux	2	63	60	1:20
$C_6H_5CH_2-Cl$	50% NaOH	Toluene	Reflux	3	58	50	1:40
$EtOOCCH_2-Br$	K_2CO_3	Toluene	Reflux	3	63	55	1:20
$EtOOCCH_2-Br$	K_2CO_3	Toluene	Reflux	3	53	38	1:40

As a conclusion, BBDE Cl can be used in a great variety of phase transfer reactions, producing in some of them the same yields as other well-stablished catalysts. It is soluble in all concentrations in water (20oC) and somewhat less soluble in dichloromethane and chloroform (17 g/100 ml, 20° C) or acetonitrile (3 g/100 ml, 20° C). In toluene or benzene, its solubility dramatically changes from 20° C (0.2 g/100 ml) to reflux temperature (30 g/100 ml for toluene) so processes performed in these solvents should be carried out at reflux temperature so that, on cooling the mixture, the final product recovered practically uncontaminated with the catalyst. Moreover, as it has been shown by the experiments described with dinucleophiles, the catalyst can be efficiently used at low concentrations with high yields.

Simultaneously with the preparation of this paper, M. Lissel et al.[40] have published the first results of the extraction of different anions by related bis-quaternary ammonium salts, using a similar concept.

EXPERIMENTAL

Melting points were determined on a Büchi SMP-20 and are uncorrected. Ir spectra were recorded on Perkin Elmer 700 and 881 spectrophotometers. ^{1}H-Nmr spectra were obtained on Varian T-60 and FT-80A instruments using TMS as internal reference. All new compounds prepared gave satisfactory analytical results. Reagents and solvents were all commercially available and were purified by standard procedures.

1,5-Bis-(N,N-diethylamino)diethylether 4. To a solution of 10 ml of water with 300 mg of TEBA Cl, and 12 g of NaOH, 2.93 g of 2-diethylaminoethanol (25 mmol) in 35 ml of methylene chloride were added with stirring. Then, 7.95 g of 2-diethylaminoethyl chloride hydrochloride (38 mmol) were added in portions, and all the mixture was refluxed with stirring for 10 hours. Then, the reaction mixture was filtered, and the solid residue was washed with 5 ml of methylene chloride. The organic phase was separated, washed with 2x30 ml of water, dried (Na_2SO_4), and passed through a active charcoal/supercell column (5 and 0.5 g respectively) eluting with 30 ml of methylene chloride. Finally, the organic solution was concentrated, and the residue was distilled in vacuo (114-117° C/13 mmHg) to afford 4.5 g (83%) of the ether **4**. The elemental analysis was performed on the dicitrate obtained as follows: 2.68 g (10 mmol) of pure **4** and 4.76 g (20 mmol) of anhidrous citric acid were suspended in 15 ml of dry ethyl acetate and 38 ml of absolute ethanol. The mixture was

stirred at room temperature for 2 h, precipitating a white solid. Mp 140–143° C. Anal. Calcd. for $C_{24}H_{44}N_2O_{15}$: C, 47.99; H, 7.38; N, 4.66. Found: C, 47.69; H, 7.69; N, 4.29 %.
Ir ν_{max} (KBr) : 2960, 2940, 2880, 2800, 1460, 1380, 1370, 1300, 1200, 1120, 1080, 1070 cm^{-1}.
^{1}H-Nmr δ ($CDCl_3$): 3.5(t, 4H), 2.6(q, 12H), 1.0(t, 12H) ppm.

1,5-Bis-(N,N-diethyl-N-benzylammonium)diethylether dichloride 5. 4 g of the ether **4** (18.5 mmol) were dissolved in 40 ml of acetone and 8 ml of benzyl chloride were added, and the mixture was refluxed with stirring for 24 hours. Then, the solid was filtered and washed with 3x20 ml of acetone, and recrystallised in acetonitrile (7.5 g, 86%), mp 190–191° C. Anal. Calcd. for $C_{26}H_{42}N_2OCl_2$: C, 66.50; H, 9.02; N, 5.97;. Found: C, 66.32; H, 9.36;N, 5.77 %.
Ir ν_{max} (KBr): 3440, 3000, 1630, 1460, 1400, 1120, 1080, 1040, 1010, 760, 710 cm^{-1}.
^{1}H-Nmr δ ($CDCl_3$) : 7.7(s, 10H), 4.7(s, 4H), 4.2(m, 4H), 3.3–3.7(m, 12H), 1.5(t, 12H) ppm.

1,3-Bis-(benzyloxy)benzene 11. To a mixture of 1.1 g of resorcine (10 mmol), 5.06 g of benzyl chloride (40 mmol) and 0.11 g of BBDE Cl (0.25 mmol) were added 25 ml of 50% aqueous solution of NaOH, and the reaction was stirred at 80° C for 15 h. Then, the organic phase was separated, and the aqueous one was extracted with 3x50 ml of methylene chloride. All organic fractions were mixed, washed with water until neutral, dried ($MgSO_4$) and evaporated to give a yellow oil which was recrystallized in hexane, giving 1.7 g (57 %) of the title compound; mp 60–64° C [36].
Ir ν_{max} (KBr): 3035, 2916, 2872, 1593, 1485, 1446, 1285, 1215, 1177, 1007 cm^{-1}
^{1}H-Nmr δ ($CDCl_3$) : 7.40(s, 10H), 7.32(d, 1H), 6.59(s, 2H), 6.50(s, 1H), 4.98(s, 4H) ppm.

3,3-Bis-(p-benzyloxyphenyl)phtalide 13. To a mixture of 0.31 g of phenolphtalein (1 mmol) 0.506 g of benzyl chloride (4 mmol) and 11 mg of BBDE Cl (0.025 mmol) in 2 ml of toluene, 2.5 ml of 50 % aqueous solution of NaOH were added, and the reaction was refluxed with stirring for 5 h. Then, the organic phase was separated, and the aqueous one was extracted with 3x5 ml of CH_2Cl_2. All organic fractions were mixed, washed with water until neutral, dried ($MgSO_4$) and evaporated to give yellow prisms which were recrystallised in acetonitrile, giving 0.36 g (74 %) of the title compound, mp 156–160° C [37].
Ir ν_{max} (KBr):3034, 2930, 1756, 1608, 1461, 1397, 1298, 1251, 1178, 1104 cm^{-1}.
^{1}H-Nmr δ ($CDCl_3$):7.07–7.49(m, 8H), 7.25(s, 10H), 6.84(d, 4H), 4.92(s, 4H) ppm.

2,2-Bis-(p-benzyloxyphenyl)propane 15. To a mixture of 0.22 g of 2,2-bis-(p-hydroxyphenyl)propane (1 mmol), 0.506 g of benzyl chloride (4 mmol) and 11 mg of BBDE Cl (0.025 mmol) in 2 ml of toluene, 2.5 ml of 50 % aqueous solution of NaOH were added, and the reaction was refluxed with stirring for 2 h. Then, the organic phase was separated, and the aqueous one was extracted with 3x5 ml of methylene chloride. All organic fractions were mixed, washed with water until neutral, dried ($MgSO_4$) and evaporated to give white prisms which were recrystallized in hexane, yielding 0.25 g (63 %) of **15**; mp 125-126° C [38].
Ir ν_{max} (KBr): 3061, 3032, 2955, 2927, 1605, 1508, 1241, 1178, 1142 cm^{-1}.
^{1}H-Nmr δ ($CDCl_3$): 7.74 (s, 10H), 7.05 (d, 2H), 6.87 (d, 2H), 4.99 (s, 4H), 1.62 (s, 6H) ppm.

2,2-Bis-(p-ethoxycarbonylmethoxyphenyl)propane 16. To a mixture of 0.22 g of 2,2-bis-(p-hydroxyphenyl)propane (1 mmol), 0.66 g of ethyl bromide (4 mmol) and and 23 mg of BBDE Cl (0.05 mmol) in 3 ml of toluene, 1.38 g of anh. K_2CO_3 were added, and the reaction was refluxed with stirring for 3 h. Then, the mixture was filtered, and the solid residue was extracted with 2x5 ml of CH_2Cl_2. All organic fractions were mixed, washed with water until neutral, dried ($MgSO_4$) and evaporated to give a yellow oil which solidified and was recrystallized in hexane, yielding 0.25 g (63 %) of the title compound; mp 72-73° C [38].
Ir ν_{max} (KBr): 3064, 2966, 2872, 1759, 1611, 1440, 1304, 1182, 1076 cm^{-1}.
^{1}H-Nmr δ ($CDCl_3$): 7.03 (d, 4H), 6.80 (d, 4H), 4.55 (s, 4H), 4.19 (q, 4H), 1.61 (s, 6H), 1.28 (t, 6H).

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REFERENCES.

1. Starks, C. M. J. Am. Chem. Soc. **1971**, 93, 195.
2. Starks, C. M. J. Am. Chem. Soc. **1973**, 95, 3613.
3. Jones, A. R. Aldrichim. Acta **1976**, 9, 35.

4. Gokel, G. W.; Weber, W. P. J. Chem. Educ. 1978, 55, 350 and 429.
5. Sjoberg, K. Aldrichim. Acta 1980, 13, 55.
6. Reuben, B.; Sjoberg, K. Chem. Tech. 1981, 315.
7. Cocagne, P.; Gallo, R.; Elguero, J. Heterocycles 1983, 20, 1379.
8. Gallo, R.; Makosza, M.; Dou, H. J. M.; Hassanaly, P. Adv. Heterocycl. Chem. 1984. 36, 176.
9. Liotta, C.; Starks, C. M. "Phase Transfer Catalysis", Academic Press, New York, 1977.
10. Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis", Springer-Verlag, N. York, 1977.
11. Keller, W. E."Phase Transfer Reactions", Fluka AG CH-9470 Buchs, 2 vols, 1986-87.
12. Dehmlow, E. V.; Dehmlow, S. "Phase Transfer Catalysis", Verlag Chemie, Weinheim, 2nd Ed., 1983.
13. Gokel, G. W.; Jarvis, B. B. "Medium Effects in Organic Synthesis", American Chemical Society Audio Course, 1983.
14. Idoux, J. P.; Wysocki, R.; Young, S.; Turcot, J.; Ohlman, C.; Leonard, R.; Synth. Commun., 1983, 13, 139.
15. Idoux, J. P.; Gupton, J. T. "Phase Transfer Catalysis. New Chemistry Catalysis and Applications", Starks, C. M. Ed., American Chemical Society, Washington 1987, 169.
16. Brunelle, D. J. in Ref. 15, 45.
17. Sunkel, C.; Fau de Casa-Juana, M.; Dorrego, F.; Pando, B.; Alvarez-Builla, J.; Vaquero, J. J.; Galera, C.; Vazquez, M. L. Brit. Pat. 2 198 725.
18. Sunkel, C.; Fau de Casa-Juana, M.; Dorrego, F.; Pando, B.; Alvarez-Builla, J.; Vaquero, J. J.; Galera, C.; Vazquez, M. L. Eur. Pat. 267 136.
19. Komeih-Zadeh, H.; Dou, H. J. M.; Metzger, J. J. Org. Chem., 1978, 43, 156.
20. Gajda, T.; Zwierzak, A. Synthesis, 1981, 1005.
21. Barco, A.; Benetti, S.; Pollini, G. P. Synthesis, 1976, 124.
22. Nishi, H.; Kohno, H.; Kano, T. Bull. Chem. Soc. Jpn., 1981, 54, 1897.
23. Claramunt, R. M.; Elguero, J.; Garcerán, R. Heterocycles, 1985, 23, 2895.
24. Dou, H. J. M.; Metzger, J. Bull. Soc. Chim. Fr., 1976, 1861.
25. McKillop, A.; Fiand, J. C.; Hug, R. P. Tetrahedron , 1974, 30, 1379.
26. Freedman, H. H.; Dubois, R. A. Tetrahedron Lett., 1975, 3251.
27. Flesia, E.; Nougier, R.; Surzur, J. M. Tetrahedron Lett., 1979, 197.
28. Holmberg, K.; Hansen, B. Tetrahedron Lett., 1975, 2303.
29. Landini, D.; Rolla, F. Synthesis, 1974, 565.
30. Reeves, W. P.; White, M. R.; Bier, D. J. Chem. Ed., 1978, 55, 56.
31. Dryanska, V.; Ivanov, C. Tetrahedron Lett., 1975, 3519.

32. Jonczyk, A.; Fedorynski, M.; Makosza, M. Tetrahedron Lett., 1972, 2395.
33. Dehmlow, E. W. Tetrahedron, 1972, 28, 175.
34. Herriott, A. W.; Picker, D. Tetrahedron Lett., 1974, 1511.
35. Coloma, S.; Fornasier, R. Synthesis, 1975, 531.
36. Takahata, H.; Omishi, Y.; Takeara, H.; Tsuritani, K.; Yamazaki, T. Chem. Pharm. Bull., 1981, 29, 1063.
37. Rowe, E. J.; Kaufman, K. L. J. Org. Chem., 1958, 23, 1622.
38. Kaufman, H. P. Arch. Pharm., 1929, 267, 212.
39. Yohe, G. R.; Vitcha,J. F. J. Am. Chem. Soc., 1935, 57, 2259.
40. Lissel, M.; Feldman, D.; Nir, M.; Rabinovitz, M. Tetrahedron Lett., 1989, 30, 1683.