Two Way Reactivity of 1,1-Dichloro-2-(chloromethyl)cyclopropane in Basic Medium: A Simple Synthesis of 1,1-Bis(aryloxy)-2-methylenecyclopropanes[1]

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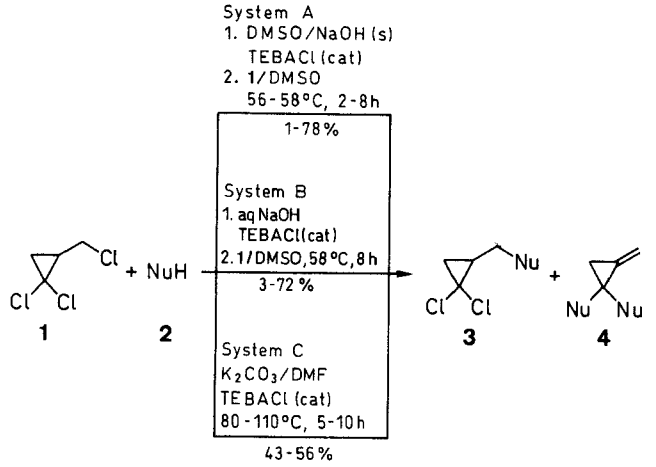
1,1-Dichloro-2-(chloromethyl)cyclopropane (**1**) reacts with phenols **2a–l**, alcohols **2m,n** or thiophenol (**2o**) in different base/solvent systems, to form either 2-(aryloxymethyl)-1,1-dichlorocyclopropanes **3** and/or 1,1-bis(aryloxy)-2-methylenecyclopropanes **4**. Reaction of **1** with piperidine (**2p**) and sodium cyanide (**2q**) affords 1,1-dichloro-2-(piperidinomethyl)cyclopropane (**3p**) and 1,1-dichloro-2-(cyanomethyl)cyclopropane (**3q**), respectively. The kind of the products formed depends on the reaction conditions and the structure of the heteronucleophile.

Some years ago, we reported that 1,1-dichloro-2-(chloromethyl)cyclopropane (**1**) reacts with nucleophiles generated from **2a,n,o** to give either products **3** and/or **4** (Scheme 1). There is some evidence that compounds **4** are formed from **1** via series of elimination–addition reactions.[2] The reaction of the structurally related 2-(bromomethyl)-1,1-dichlorocyclopropane with some phosphorus, sulfur and nitrogen nucleophiles afforded exclusively products **3**.[3] The compounds of the general structure **3** are considered to be potential plant protection substances.[4] Recently, we have described chemical transformations of 1-bromo-2-(chloromethyl)cyclopropane by means of nucleophiles.[5]

We wish now to detail results on chemical transformations of **1** by means of heteroanions generated from phenol (**2a**), its ring-substituted derivatives **2b–k**, 1-naphthol (**2l**), two alcohols **2m,n**, thiophenol (**2o**), as well as by means of piperidine (**2p**) and sodium cyanide (**2q**), Scheme 1.

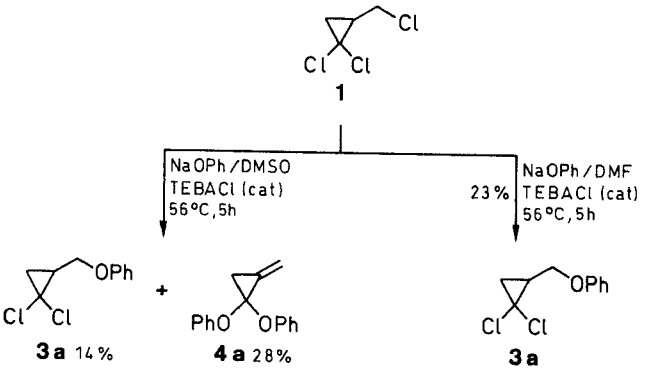


2–4	Nu	2–4	Nu	2–4	Nu
a	PhO	g	2-MeC_6H_4O	m	MeO
b	2-ClC_6H_4O	h	3-MeC_6H_4O	n	BnO
c	3-ClC_6H_4O	i	4-MeC_6H_4O	o	PhS
d	4-ClC_6H_4O	j	2,4-$Me_2C_6H_3O$	p	$(CH_2)_5N$
e	2,4-$Cl_2C_6H_3O$	k	4-$MeOC_6H_4O$	q	CN
f	2,5-$Cl_2C_6H_3O$	l	1-$C_{10}H_7O$		

Scheme 1

The following base–solvent systems were chosen for the generation of these heteroanions: A – solid sodium hydroxide/dimethyl sulfoxide (DMSO)/benzyltriethylammonium chloride (TEBACl) catalyst, B – 50% aqueous sodium hydroxide/DMSO/TEBACl catalyst and C – solid potassium carbonate/dimethylformamide (DMF)/TEBACl catalyst. An experiment with **2a** and **1** carried out in the system A with and without TEBACl catalyst gave pure **4a** with yields of 36% and 27%, respectively. Hence all reactions were performed with TEBACl. A similar, expedient effect of TEBACl on carbanionic reactions carried out in solid potassium hydroxide/DMSO systems, has already been noticed.[6] Preliminary experiments have shown that the mixtures practically did not contain **1** after reactions carried out in system A or B. Stirring of **1** in system A without a heteronucleophile for 1 hour, induced an exothermic reaction with consumed a substantial amount of **1** with the formation of some products (GC) and a tarry material. To minimize these undesired processes, practically all reactions were carried out with an excess of **2** (**2/1** ~ 3). Nevertheless, the yields of **3** and **4** usually did not exceed 50%. The results of reactions of **1** with phenols **2a–l** are collected in Tables 1 and 2.

It is evident that the kind of the products formed depends on the reactions conditions, and the structure of **2**. While in system A or B (solid, or conc. aqueous solution of sodium hydroxide) mixtures of products **3** and **4** are usually formed, system C afforded nearly exclusively chain substituted products **3** (Scheme 1). To gain more information on these reactions, we synthesized sodium phenolate, and allowed it to react with **1** in DMSO or DMF (Scheme 2).



Scheme 2

A specific solvent effect arises from these experiments. Again in DMF the product **3a** is formed, while in DMSO a mixture of **3a** and **4a**, is obtained, in which the latter prevails. Evidently, in the latter solvent phenolate beha-

Table 1. Yields of Products **3** and **4** from the Reactions of **1** with Phenols **2** Determined by GC and/or ^{1}H NMR

2–4	Base/solvent System[a]	Temp. (°C)	Time (h)	Yield (%)	
				3	4
a	B	58	8[b]	3[c]	39[c]
b	A	58	5	21[c]	15[c]
c	A	58	6	16[c]	7[c]
d	A	58	6[d]	7[e]	35[e]
e	A	58	8	28[c]	~1[c]
g	A	56	5	6[f]	46[f]
h	A	58	5	33[f]	14[f]
i	A	56	6	2[e]	46[e]
j	A	58	8	4[c]	27[c]
k	A	58	8	48[c]	23[c]

[a] A: solid NaOH/DMSO/TEBACl (cat); B: 50% aq NaOH/DMSO/TEBACl (cat).
[b] After 2 h the yield of **4a** was 17%.
[c] Determined by ^{1}H NMR.
[d] After 2 h the yield of **4d** was 11%.
[e] Determined by GC.
[f] Determined by ^{1}H NMR and by GC.

ves partially as a base to transform **1** into 1,1-dichloro-2-methylenecyclopropane which further affords **4**.[2] We assume that in system A or B, sodium hydroxide also acts as a base towards **1**. Relatively low yields of **3a–l** and **4a–l** are undoubtedly due to the above mentioned instability of **1** in basic medium. Decomposition of final products is less probable, since in the experiments with **2a** or **2d** the yields of **4a** or **4d** increased in time (Table 1).

The two alcohols methanol **(2m)** and benzyl alcohol **(2n)** were also tried in reaction with **1**. In the first case, a fairly complex mixture of products was formed, from which **4m** was isolated by careful fractional distillation (Table 2). On the other hand, the reaction of **2n** with **1** in system A did not give products of the structure **3** or **4**. Instead, a high-boiling material was isolated, which was not characterized further. We found that the reaction of an excess of **2n** with **1**, carried out in the presence of sodium hydride afforded **3n** with low yield (Table 2). Its structure was proved by comparison with a sample prepared via an independent route (see Experimental Section). Therefore, reactions of alkoxides with **1** resulted in the formation of complex products mixtures, difficult to separate.

Two sulfur and nitrogen nucleophiles, thiophenol **(2o)** in system A, and piperidine **(2p)** without any external base, showed their high nucleophilicity in reactions with **1**. In these cases, the products **3o** and **3p** were formed in high yield, respectively (Table 2). A crystalline quaternary salt with methyl iodide was smoothly prepared from the latter product.

Finally the reaction of sodium cyanide with **1** in DMSO gave **3q** in good yield.

^{1}H NMR spectra of **4** show two characteristic triplets at δ = 5.0–6.0 (J = 2.5 Hz), and at δ = 5.7–6.3 (J = 3.2 Hz) for magnetically non-equivalent CH_2=C protons, and a doublet of doublets (sometime poorly separated even after expansion) at δ = 1.6–2.2 for CH_2 of cyclopropane, with the same two J values. Such a pattern unequivocally indicates 1,1-(gem) rather than 1,2-disubstitution in **1** by nucleophiles, to give **4**.

To summarize, we showed a twofold reactivity of **1** which depends on reaction conditions and the structure of the nucleophile **2**. Furthermore, we described a simple method for the preparation of synthetically interesting compounds **4**.

All reagents and solvents were of commercial quality, DMSO and DMF were distilled before use. NaOH was ground on a ball mill. The starting cyclopropane **1**,[7] sodium phenoxide[8] and allyl benzyl ether[9] were prepared according to literature procedures. 2-(Benzyloxymethyl)-1,1-dichlorocyclopropane was synthesized from allyl benzyl ether and $CHCl_3$ under PTC conditions;[10] yield 44%; bp 100–102 °C/0.5 Torr.

$C_{11}H_{12}Cl_2O$ (231.1) calc. C 57.17 H 5.23 Cl 30.68
found 56.98 5.18 30.35

^{1}H NMR ($CDCl_3$): δ = 1.15–2.30 (m, 3H, $CH_2CH_{cyclopropyl}$), 3.88–4.16 (m, 2H, CH_2O), 4.96–5.13 (m, 2H, CH_2Ar), 7.85–8.45 (m, 5 H_{arom}).

Melting points and boiling points are uncorrected. Column chromatography (CC) was performed on Merck silica gel MN 60 (70–270 mesh), eluting with hexane/EtOAc (gradient). GC analyses were carried out on a Chromatron GCHF 18.3 gas chromatograph using an OV 17 column (5% silicon oil OV 17 on Chromosorb W) and flame-ionization detector with N_2 as the carrier gas. Mass spectra were recorded on a LKB 2091 spectrometer.

^{1}H NMR spectra were recorded on a Bruker-Spectrospin spectrometer at 100 MHz as solutions in $CDCl_3$ with TMS as internal standard.

Dichlorocyclopropanes 3 and Methylenecyclopropanes 4; General Procedures:

System A: DMSO (15 mL), powdered NaOH (4.8 g, 120 mmol), TEBACl (0.1 g, 0.44 mol) and the corresponding OH or SH acid (60 mmol) were stirred until the thermal effect ceased. Then the solution of **1** (3.2 g, 20 mmol) in DMSO (10 mL) was added and the reaction was stirred at the temperature and for the time indicated in Table 1 and 2. After cooling, the mixture was poured into H_2O (ca. 250 mL) and extracted with $CHCl_3$ or CH_2Cl_2 (3 × 150 mL). The organic extracts were washed with 20% aq. NaOH (150 mL) and H_2O, dried ($MgSO_4$) and concentrated on a rotary evaporator. The residue was purified as reported in Table 1 and 2.

System B: To 50% aq NaOH (25 mL), TEBACl (0.1 g, 0.44 mmol) and OH or SH acid (60 mmol) the solution of trichloro compound **1** (3.2 g, 20 mmol) in DMSO (10 mL) was added (thermal effect) and the mixture was stirred at the temperature and for the time indicated in Table 1 and 2. Then the mixture was poured into H_2O (ca. 250 mL), the solid product was filtered off and the liquid one was extracted with $CHCl_3$ (3 × 150 mL) and worked up as described for system A (Tables 1, 2).

System C: Powdered K_2CO_3 (6.0 g, 43 mmol), DMF (40 mL) or DMF/acetone (1:1, 40 mL), TEBACl (0.1 g, 0.44 mmol), **1** (3.2 g, 20 mmol) and the corresponding phenol **2** (60 mmol) (Table 2) were stirred and heated at the temperature and for the time indicated in Table 2. The mixture was then cooled, poured into H_2O (ca. 250 mL), extracted with $CHCl_3$ (3 × 150 mL) and worked up as described for system A (Table 2).

2-(Benzyloxymethyl)-1,1-dichlorocyclopropane (3n):

NaH (3.6 g, 150 mmol) (mineral oil was washed out with hexane) and BnOH (**2n**; 16.2 g, 150 mmol) were stirred until the thermal effect ceased. Trichloro compound **1** (8.0 g, 50 mmol) was added, the mixture was stirred at 80 °C for 4 h, cooled, then poured into H_2O (ca. 250 mL), and worked up as described for system A (Table 2). Product **3n** was identified by comparison (GC, ^{1}H NMR) with an authentic sample.

Table 2. Pure Products **3** and **4** from the Reactions of **1** with **2**

Product	Conditions			Method of isolation[b]	Yield (%)	bp (°C)/Torr or mp (°C) (solvent)	Molecular Formula[c]	MS (70 eV) *m/z* (%)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)
	System[a]	Temp. (°C)	Time (h)						
3a	C	110	6	I	46	130/0.1 (Kugelrohr) 35–36 (EtOH)	$C_{10}H_{10}Cl_2O$ (217.0)	–	1.35–1.43, 1.63–1.81 (m, 2H, $CH_{2\,cyclopropyl}$), 1.96–2.27 (m, 1H, CH), 4.05–4.12 (m, 2H, CH_2O), 6.87–7.37 (m, $5H_{arom}$)
4a	A	56	6	II	36	98–100 (MeOH)	$C_{16}H_{14}O_2$ (238.2)	237 (M-1, 13), 145 (50), 117 (100), 94 (27), 77 (56), 65 (17), 51 (39)	1.98 (dd, 2H, J = 2.50, 3.15, $CH_{2\,cyclopropyl}$), 5.54 (t, 1H, J = 2.47, =CH), 5.86 (t, 1H, J = 3.20, =CH), 6.99–7.33 (m, $10H_{arom}$)
3b	A	58	5	III	15	120/0.1 (Kugelrohr)	$C_{10}H_9Cl_3O$ (251.5)	–	1.38–1.44, 1.71–1.77 (m, 2H, $CH_{2\,cyclopropyl}$), 2.11–2.20 (m, 1H, CH), 4.09–4.24 (m, 2H, CH_2O), 6.81–7.69 (m, $4H_{arom}$)
4b	A	58	5	IV	7	71–73 (EtOH)	$C_{16}H_{12}Cl_2O_2$ (307.2)	–	2.08 (dd, 2H, J = 2.52, 3.20, $CH_{2\,cyclopropyl}$), 5.60 (t, 1H, J = 2.49, =CH), 5.90 (t, 1H, J = 3.18, =CH), 6.99–7.66 (m, $8H_{arom}$)
3c	A	58	6	III	14	111/0.1 (Kugelrohr)	$C_{10}H_9Cl_3O$ (251.5)	–	1.37–1.42, 1.74–1.80 (m, 2H, $CH_{2\,cyclopropyl}$), 2.07–2.18 (m, 1H, CH), 4.03–4.15 (m, 2H, CH_2O), 6.85–7.22 (m, $4H_{arom}$)
4c	A	58	6	III	6	130/0.1 (Kugelrohr)	$C_{16}H_{12}Cl_2O_2$ (307.2)	–	2.03 (dd, 2H, J = 2.53, 3.24, $CH_{2\,cyclopropyl}$), 5.61 (t, 1H, J = 2.48, =CH), 5.92 (t, 1H, J = 3.21, =CH), 7.03–7.27 (m, $8H_{arom}$)
3d	C	110	5	III	56	125/0.05 (Kugelrohr)	$C_{10}H_9Cl_3O$ (251.5)	–	1.25–1.44, 1.56–1.83 (m, 2H, $CH_{2\,cyclopropyl}$), 1.91–2.26 (m, 1H, CH), 4.03–4.10 (m, 2H, CH_2O), 6.80–7.28 (m, $4H_{arom}$)
4d	A	58	6	I	34	200/0.05 (Kugelrohr) 62–64 (EtOH)	$C_{16}H_{12}Cl_2O_2$ (307.2)	307 (M^+, 4), 181 (22), 179 (43), 144 (22), 128 (22), 116 (100), 113 (11), 77 (11), 51 (19)	1.97 (dd, 2H, J = 2.49, 3.19, $CH_{2\,cyclopropyl}$), 5.56 (t, 1H, J = 2.50, =CH), 5.83 (t, 1H, J = 3.20, =CH), 7.06–7.31 (m, $8H_{arom}$)
3e	A	58	8	III	28	145/0.01 (Kugelrohr)	$C_{10}H_8Cl_4O$ (286.0)	–	1.41–1.46, 1.75–1.81 (m, 2H, $CH_{2\,cyclopropyl}$), 2.12–2.21 (m, 1H, CH), 4.10–4.21 (m, 2H, CH_2O), 6.85–7.54 (m, $3H_{arom}$)
3f	A	58	8	V	38	115/0.01	$C_{10}H_8Cl_4O$ (286.0)	–	1.42–1.47, 1.75–1.81 (m, 2H, $CH_{2\,cyclopropyl}$), 2.13–2.19 (m, 1H, CH), 4.14–4.18 (m, 2H, CH_2O), 6.89–7.79 (m, $3H_{arom}$)
4g	A	56	5	I	40	165/0.2 (Kugelrohr) 51–53 (MeOH)	$C_{18}H_{18}O_2$ (266.3)	–	1.99 (dd, 2H, J = 2.52, 3.18, $CH_{2\,cyclopropyl}$), 5.53 (t, 1H, J = 2.46, =CH, 5.88 (t, 1H, J = 3.21, =CH), 6.90–7.51 (m, $8H_{arom}$)
4h	A	58	5	VI	5	oil	$C_{18}H_{18}O_2$ (266.3)	–	2.02 (dd, 2H, J = 2.46, 3.15, $CH_{2\,cyclopropyl}$), 5.57 (t, 1H, J = 2.46, =CH), 5.90 (t, 1H, J = 3.18, =CH), 6.68–7.21 (m, $8H_{arom}$)
3i	C[d]	80	10	III	43	140/0.1 (Kugelrohr)	$C_{11}H_{12}Cl_2O$ (231.1)	–	1.26–1.43, 1.55–1.81 (m, 2H, $CH_{2\,cyclopropyl}$), 1.95–2.21 (m, 1H, CH), 2.29 (s, 6H, $ArCH_3$), 4.04–4.11 (m, 2H, CH_2O), 6.78–7.24 (m, $8H_{arom}$)
4i	A	56	6	III	42	118/0.05 (Kugelrohr)	$C_{18}H_{18}O_2$ (266.3)	265 (M-1, 10), 159 (72), 158 (35), 144 (11), 131 (100), 108 (42), 107 (27), 91 (75), 77 (25), 65 (25), 53 (10)	1.94 (dd, 2H, J = 2.49, 3.15, $CH_{2\,cyclopropyl}$), 2.27 (s, 6H, $ArCH_3$), 5.50 (t, 1H, J = 2.46, =CH), 5.82 (t, 1H, J = 3.18, =CH), 7.08–7.21 (m, $8H_{arom}$)
4j	A	58	8	III	27	175/0.05 (Kugelrohr)	$C_{20}H_{22}O_2$ (294.4)	–	2.02 (dd, 2H, J = 2.52, 3.18, $CH_{2\,cyclopropyl}$), 2.21 [s, 6H, $Ar(CH_3)_2$], 2.33 [s, 6H, $Ar(CH_3)_2$], 5.58 (t, 1H, J = 2.50, =CH), 5.92 (t, 1H, J = 2.16, =CH), 6.99–7.46 (m, $6H_{arom}$)

Table 2. (continued)

Product	Conditions			Method of isolation[b]	Yield (%)	bp (°C)/Torr or mp (°C) (solvent)	Molecular Formula[c]	MS (70 eV) *m/z* (%)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)
	System[a]	Temp. (°C)	Time (h)						
3k	C	110	8	III	45	180/0.2 (Kugelrohr)	$C_{11}H_{12}Cl_2O_2$ (247.1)	–	1.33–1.38, 1.69–1.75 (m, 2H, $CH_{2\,cyclopropyl}$), 2.04–2.14 (m, 1H, CH), 3.75 (s, 3H, OCH_3), 4.03–4.06 (m, 2H, CH_2O), 6.74–7.13 (m, $4H_{arom}$)
4k	A	58	5	I	22	140/0.05 (Kugelrohr) 32–34 (EtOAc)	$C_{18}H_{18}O_4$ (298.3)	298 (M^+, 3), 175 (70), 147 (54), 124 (45), 121 (100), 91 (26), 77 (31), 64 (23)	1.92 (dd, 2H, *J* = 2.49, 3.18, $CH_{2\,cyclopropyl}$), 3.74 (s, 6H, $ArOCH_3$), 5.50 (t, 1H, *J* = 2.46, =CH), 5.77 (t, 1H, *J* = 3.18, =CH), 7.06–7.29 (m, $8H_{arom}$)
4l	A	58	8	II	32	109–110 (MeOH)	$C_{24}H_{18}O_2$ (338.4)	–	2.21 (dd, 2H, *J* = 2.52, 3.16, $CH_{2\,cyclopropyl}$), 5.63 (t, 1H, *J* = 2.50, =CH), 6.05 (t, 1H, *J* = 3.19, =CH), 7.26–8.26 (m, $14H_{arom}$)
4m	A	58	2	VII	22	112/760	$C_6H_{10}O_2$ (114.2)	–	1.61 (dd, 2H, *J* = 2.77, 3.05, $CH_{2\,cyclopropyl}$), 3.80 [s, 6H, $(CH_3)_2$], 5.96 (t, 1H, *J* = 2.77, =CH), 6.32 (t, 1H, *J* = 3.07, =CH)
3n	[e]	80	4	VIII	15	125/0.5 (Kugelrohr)	$C_{11}H_{12}Cl_2O$ (231.1)	–	1.16–2.23 (m, 3H, $CH_2CH_{cyclopropyl}$), 3.47–3.78 (m, 2H, CH_2O), 4.35–4.82 (m, 2H, CH_2Ar), 7.03–7.59 (m, $5H_{arom}$)
3o	A	20	1	IX	78[f]	110/0.1	$C_{20}H_{10}Cl_2S$	–	1.12–1.17, 1.56–1.62 (m, 2H, $CH_{2\,cyclopropyl}$), 1.77–1.82 (m, 1H, CH), 2.84–3.19 (m, 2H, CH_2O), 7.18–7.39 (m, $5H_{arom}$)
3p	[g]	100	1	IX	61	105/0.1	$C_9H_{15}Cl_2N$	–	1.34–1.75 (m, 9H, $CH_2CH_2CH_2$, $CH_2CH_{cyclopropyl}$), 2.34–2.59 (m, 6H, CH_2NCH_2 and NCH_2)
3q	[h]	58	6	IX	67	80/0.1	$C_5H_5Cl_2N$	–	1.28–1.97 (m, 3H, $CH_2CH_{cyclopropyl}$), 2.52–2.74 (m, 2H, CH_2CN)

[a] A: solid NaOH/DMSO/TEBACl (cat); B: 50% aq NaOH/DMSO/TEBACl (cat); C: solid K_2CO_3/DMF/TEBACl (cat).

[b] I: the product was isolated by CC, then vacuum distilled on Kugelrohr and crystallized; II: the product was isolated by crystallization; III: the product was isolated by CC and then vacuum distilled on Kugelrohr; IV: the product was isolated by CC and crystallized; V: the product was isolated by CC and then vacuum distilled; VI: the product was isolated by CC; VII: the product was isolated by distillation on Fisher column; VIII: the excess of nucleophile was removed by vacuum distillation, the residue was purified by CC and then vacuum distilled on Kugelrohr; IX: the product was isolated by vacuum distillation.

[c] Satisfactory microanalyses obtained: C ± 0.28, H ± 0.23, N ± 0.14, Cl ± 0.33, S ± 0.37, exception **4j** C ± 0.55.

[d] Mixture of DMF/acetone (1 : 1) was used.

[e] NaH was used.

[f] In system B, the yield of **3o** is 72%.

[g] Excess of piperidine was used.

[h] Reaction was carried out in DMSO.

1,1-Dichloro-2-(piperidinomethyl)cyclopropane (3p):
Piperidine (**2p**; 10.2 g, 120 mmol) and **1** (6.4 g, 40 mmol) were stirred and refluxed (ca. 100 °C) for 1 h. The mixture was poured into H_2O (ca. 250 mL), excess of 20% aq NaOH was added and the product was extracted with $CHCl_3$ (3 × 100 mL). The organic layers were washed with brine and worked up as described for system A (Table 2).

1-(2,2-Dichlorocyclopropyl)-1-methylpiperidinium Iodide (3p · MeI):
Amine **3p** (0.7 g, 3.4 mmol) and MeI (0.97 g, 0.44 mL, 6.8 mmol) were stirred. After a few minutes, exothermic reaction starts, and an oily layer was separated. The volatile compounds were evaporated on a rotary evaporator, and the residue was crystallized from EtOH to give **3p** · MeI; yield 0.98 g (82%); mp 154–156 °C.

$C_{10}H_{18}NCl_2I$ (350.1)	calc.	C 34.31	H 5.18	N 4.00
	found	34.45	5.32	4.00

^{1}H NMR ($CDCl_3$): δ = 1.66–2.27 (m, 9H, $CH_2CH_2CH_2$, $CH_2CH_{cyclopropyl}$), 3.46 (s, 3H, CH_3), 3.62–3.69 (m, 1H, NCH), 3.74–3.87 (m, 4H, CH_2NCH_2), 4.24–4.37 (m, 1H, NCH)

1,1-Dichloro-2-(cyanomethyl)cyclopropane (3q):
DMSO (20 mL), NaCN (2.95 g, 60 mmol), TEBACl (0.1 g, 0.44 mmol) and **1** (3.2 g, 20 mmol) were stirred at ca. 58 °C for 6 h. The mixture was worked up as described for system A (Table 2). Lit.[11] bp 100–104 °C/10 Torr.

Reaction of Sodium Phenolate with 1:
In DMSO/TEBACl catalyst: DMSO (15 mL), TEBACl (0.1 g, 0.44 mmol) and sodium phenolate (6.96 g, 60 mmol) were stirred and a solution of **1** (3.2 g, 20 mmol) in DMSO (5 mL) was added dropwise. The mixture was stirred until thermal effect (ca. 58 °C) ceased then at 56 °C for 5 h, cooled, and poured into H_2O (250 mL).

The solid was filtered and crystallized from MeOH to give **4a**; yield: 1.0 g (21%); mp 98–100 °C. The methanolic filtrate was concentrated, the residue was dissolved in $CHCl_3$ (10 mL), washed with 20% aq NaOH (15 mL), H_2O (3 × 20 mL), dried ($MgSO_4$) and the solvent was evaporated. The residue (0.9 g) was analyzed by GC to show **3a** (66%) and **4a** (34%). Total yield of **3a** was 14% and of **4a**, 28%. The H_2O phase after filtration of the solid material was extracted with $CHCl_3$ (3 × 30 mL), the organic extracts were washed with 20% aq NaOH and then H_2O, dried ($MgSO_4$) and the solvent was evaporated. The residue (ca. 0.1 g) was analyzed by GC to show phenol and unknown products.

In DMF/TEBACl catalyst: DMF (15 mL), TEBACl (0.1 g, 0.44 mmol) and sodium phenolate (6.96 g, 60 mmol) were stirred and a solution of **1** (3.2 g, 20 mmol) in DMF (5 mL) was added dropwise. After the thermal effect (ca. 35 °C) ceased the mixture was stirred at 56 °C for 5 h, poured into H_2O (ca. 250 mL), extracted with $CHCl_3$ (3 × 100 mL) and worked up as described for system A. The residue after evaporation of the solvent was analyzed by GC to show **3a**, and distilled to give pure **3a**; yield 1.0 g (23%); bp 90 °C/0.1 Torr.

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