Generation and Reaction of Ammonium Ylides in Basic Two-Phase Systems

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Keywords: Alkenes / Cyclopropanes / Oxiranes / Phase-transfer catalysis / Ylides

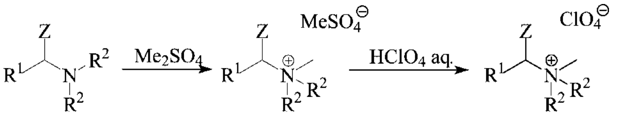
Reaction of the quaternary ammonium salts **2a**–**i** with electrophilic alkenes **3**, active alkylating agents **7** or aromatic aldehydes **11**, carried out in basic two-phase systems A–D, afforded cyclopropanes **4**, cyanoalkenes **8** or cyanooxiranes **12** respectively, via the corresponding ammonium ylides $\mathbf{2}^{+-}$. The method is very simple, and gives cyclopropanes **4** and cyanoalkenes **8** in high yield. Under similar conditions, 1-cyanodienes **8aa**,**ba** were cyclopropanated at the γ,δ-double bond with formation of vinylcyclopropanes **9a**,**b**. The stereochemistry of the prepared cyclopropanes was elucidated from literature, ^{1}H NMR spectroscopic data, NOE experiments or X-ray single crystal analysis.

Introduction

Ammonium ylides,[1] which are often generated by deprotonation of the corresponding quaternary ammonium salts, are prone to undergo sigmatropic rearrangements,[2] while their reactions with electrophiles are less systematically studied. Thus, cyanotrimethylammonium iodide generates an ylide upon treatment with NaH in THF, which then reacts with α,β-unsaturated carbonyl compounds to afford the corresponding cyclopropanes in 21–86% yield.[3] Pyridinium ylides, which are produced by treating pyridinium salts with triethylamine in ethanol or DMF, react with alkenes substituted with two electron-withdrawing groups (EWGs) to give the corresponding cyclopropanes in good yields.[4] Analogous reactions with resin-bound pyridinium salts have also been investigated.[5] The reactions of pyridinium ylides are, however, limited to strongly electrophilic alkenes. Furthermore, these ylides often behave as 1,3-dipoles towards alkenes, rather than as nucleophiles.[1,4,6] Recently, a one-pot cyclopropanation of electrophilic alkenes has been described which utilizes α-halogenocarbonyl compounds in the presence of a base and equimolar or even catalytic amounts of tertiary amines.[7] This process, when carried out with chiral amines and a base, leads to cyclopropanes with *ee*'s of up to 94%. Ammonium ylides, which were generated from quaternary ammonium salts by treatment with a base, were used to functionalize nitro aromatic compounds by vicarious nucleophilic substitution (VNS).[8]

Results and Discussion

We found that suitably substituted quaternary ammonium salts, when treated with a base, generate ylides that are useful intermediates for the preparation of cyanocyclopropanes, cyanoalkenes and cyanooxiranes.[9] To determine the scope and limitation of these reactions a series of quaternary ammonium salts **2** was synthesized by quaternization of aminonitriles **1a**–**h** or aminoester **1i** with dimethyl sulfate as a alkylating agent. The oily methyl sulfates obtained were transformed into crystalline perchlorates (**2a2**,**e**,**f**,**i**; Scheme 1).



1 **2** **2a2,e,f,i**

1, 2	R^1	R^2	R^2	Z	Counterion
a1	Ph	Me	Me	CN	$MeSO_4$
a2	Ph	$(CH_2)_4$		CN	ClO_4
a3	Ph	$(CH_2)_2O(CH_2)_2$		CN	$MeSO_4$
b	$4\text{-}MeOC_6H_4$	Me	Me	CN	$MeSO_4$
c	$4\text{-}NCC_6H_4$	Me	Me	CN	$MeSO_4$
d	$1\text{-}C_{10}H_7$	Me	Me	CN	$MeSO_4$
e	$2\text{-}C_4H_3O$	Me	Me	CN	ClO_4
f	$2\text{-}C_4H_3S$	Me	Me	CN	ClO_4
g	$Me_2C{=}CH$	Me	Me	CN	$MeSO_4$
h	(*E*)-PhCH=CH	$(CH_2)_4$		CN	$MeSO_4$
i	Ph	Me	Me	CO_2Et	ClO_4

Scheme 1.

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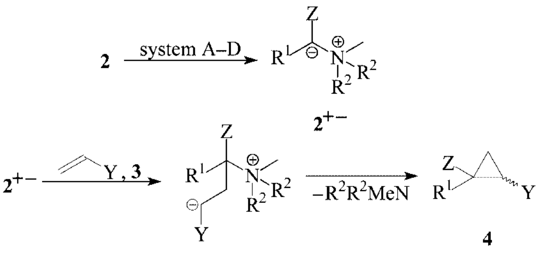
DOI: 10.1002/ejoc.200400556

The reaction of salt **2a1** with several bases in different solvents [$NaNH_2$/liq. NH_3, NaH/DMF, *t*BuOK/DMSO and 50% aq. NaOH/dichloromethane with benzyltriethylammonium chloride (TEBAC) as a phase-transfer catalyst[10–13]] revealed that ylide **2a1**$^{+-}$ is not prone to undergo sigmatropic rearrangements. These results indicate that sigmatropic rearrangements of ylides **2**$^{+-}$ should not compete with their reactions with electrophiles.

Deprotonation–alkylation of **1a1** requires rather harsh phase-transfer catalysis (PTC) conditions (mixture of conc. and solid NaOH, elevated temp.),[14] while the presence of the trimethylammonium group in **2a1** significantly decreases its pK_a, thus allowing the generation of **2a1**$^{+-}$ under the mild conditions of a typical two-phase basic system [the pK_a values of **1a1** and **2a1**, estimated from the acidity coefficients of substituents and the assumed value for methane (pK_a = 40),[15] are 20.5 and 11.5, respectively].

Preliminary experiments consisted of stirring salt **2a1** with an excess of acrylonitrile (**3a**) in the presence of 50% aq. NaOH, with TEBAC as catalyst, in toluene, diethyl ether or dichloromethane. When the reaction was carried out in the latter solvent, cyclopropane **4aa**[16–18] was isolated in 95% yield, while the product yield was rather low in the other two solvents. These results are presumably due to the limited solubility of **2a1** (and possibly **2a1**$^{+-}$) in toluene and diethyl ether.

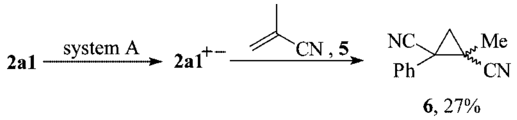
A review of the literature data concerning the generation and reactions of ylides (particularly phosphonium ones) under PTC conditions revealed that some processes are carried out with a catalyst and others without.[19] When the onium salt is deprotonated at the phase boundary of the two-phase system, the resulting ylide can dissolve in the organic phase without the aid of the catalyst. On the other hand, the onium salt itself may facilitate generation of the ylide by acting as a catalyst. Reaction of **2a1** with **3a** carried out in the presence of 50% aq. NaOH in dichloromethane without TEBAC (system A) led to formation of **4aa** in 96% yield (Scheme 2, Table 1). Since the catalyst is not required to obtain high yields of the product, all experiments in basic two-phase systems with quaternary ammonium salts **2** were carried out without a phase-transfer catalyst.



3	a	b	c	d	e	f	g
Y	CN	CO_2Me	CO_2tBu	CHO	COMe	COPh	SO_2Ph

Scheme 2.

The salt **2a1** was reacted with a series of electrophilic alkenes **3b**,**c**,**g** in system A to give cyclopropanes **4ab**,[20]**4ac**[16] and **4ag**, respectively, as mixtures of *Z* and *E* isomers in high yields (Table 1). Hydrolysis of esters in system A, observed in the case of methyl acrylate (**3b**), was prevented by the use of large amounts of dichloromethane. Under these conditions the reactions proceeded even more efficiently in system A than in system B (powdered K_2CO_3 in dichloromethane; Table 1, entries 2 and 3). Attempted synthesis of cyclopropane **4ae** from **2a1** and vinyl ketone **3e** failed in system A, while the same reaction carried out in system B gave (*Z*,*E*)-**4ae** in excellent yield. System B is also recommended for the preparation of **4ad** and **4af** from **2a1** and α,β-unsaturated carbonyl compounds **3d** and **3f**, respectively (Table 1). Methacrylonitrile (**5**) and crotononitrile were allowed to react with **2a1** in systems A and B, but only the former nitrile formed one isomer of 1,2-dicyano-1-methyl-2-phenylcyclopropane (**6**)[22] in 27% yield (Scheme 3). This reactivity pattern is not very surprising as decreased activity of α- and particularly β-substituted electrophilic alkenes in Michael reactions is well known.[23]

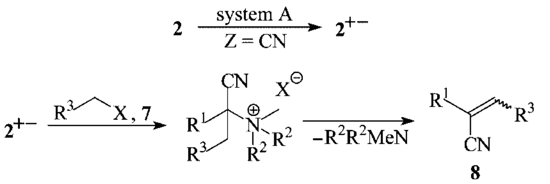


Scheme 3.

In the reactions described so far, trimethylammonium (as trimethylamine) acts as a leaving group. Salts **2a2** and **2a3**, which contain cyclic amine fragments, were allowed to react with nitrile **3a** and esters **3b**,**c** to give the corresponding cyclopropanes in equally good yields. This seems to indicate that the structure of the amine leaving group is not a significant factor controlling these reactions.

Alkenes with EWG substituents are typically prepared by Knoevenagel[24] or Wittig[25,26] reactions, or their modified versions. A procedure using sulfonium and arsonium ylides for the preparation of alkenes lacking EWGs has also been described.[27,28]

Reactions of **2a1** with active alkylating agents **7a**–**d** (usually used in excess), which were carried out in system A, resulted in the formation of four 1-cyano-1-phenyl alkenes **8aa**–**ad**[29–31] in high yields. Apparently, the alkylated quaternary ammonium salts easily undergo a Hofmann elimination reaction (Scheme 4, Table 2).



7	a	b	c	d	e
R^3	CH_2=CH	Me_2C=CH	PhCH=CH	Ph	2-C_4H_3S
X	Br	Br	Cl	Br	Cl

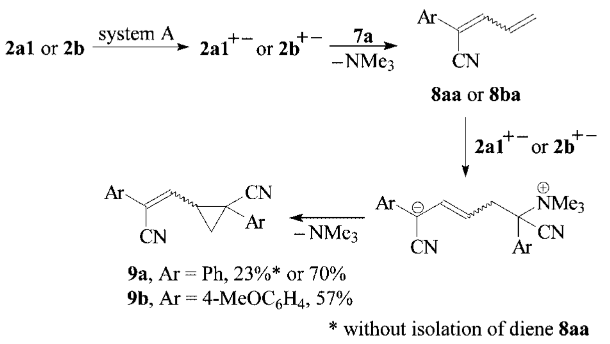
Scheme 4.

Table 1. Synthesis of cyclopropanes **4** in reactions of salts **2** with electrophilic alkenes **3** under conditions A–D

Entry	Salt	Alkene	**3/2** [mol/mol]	Time [h]	Conditions[a]	Product	Yield [%]	Isomer	*Z*/*E*[b]
1	**2a1**	**3a**	6	5	A	**4aa**[16–18]	96	*Z* + *E*	55:45[c]
2	**2a1**	**3b**	10	2	A	**4ab**[20,21]	91	*Z* + *E*	80:20
3	**2a1**	**3b**	5	5	B	**4ab**[20,21]	80	*Z* + *E*	82:18[c]
4	**2a1**	**3c**	3	7.5	A	**4ac**[16]	91	*Z* + *E*	78:22
5	**2a1**	**3d**	7	7.5	B	**4ad**	46	*Z* + *E*	62:38
6	**2a1**	**3e**	5	3.5	B	**4ae**	90	*Z* + *E*	81:19
7	**2a1**	**3f**	1	6	B	**4af**	60	*Z* + *E*	76:24
8	**2a1**	**3g**	1	6	A	**4ag**	92	*Z* + *E*	90:10
9	**2a2**	**3b**	10	4	A	**4ab**[20,21]	78	*Z* + *E*	78:22[c]
10	**2a2**	**3c**	3	5	A	**4ac**[16]	72	*Z* + *E*	80:20[c]
11	**2a3**	**3a**	6	6.5	A	**4aa**[16–18]	83	*Z* + *E*	67:33[c]
12	**2b**	**3a**	3	4	A	**4ba**	81	*Z* + *E*	50:50
13	**2b**	**3b**	10	2	A	**4bb**	84	*Z* + *E*	71:29
14	**2b**	**3b**	5	5	B	**4bb**	61	*Z* + *E*	73:27[c]
15	**2b**	**3c**	3	6	A	**4bc**	80	*Z* + *E*	76:24
16	**2b**	**3e**	5	5	B	**4be**	84	*Z* + *E*	75:25
17	**2b**	**3f**	1	5	B	**4bf**	69	*Z* + *E*	69:31
18	**2b**	**3g**	1	7	B	**4bg**	91	*Z* + *E*	83:17
19	**2c**	**3a**	3	4	A	**4ca**	46	*Z* + *E*	50:50
20	**2c**	**3b**	10	2	A	**4cb**	88	*Z* + *E*	51:49
21	**2c**	**3b**	5	5	B	**4cb**	79	*Z* + *E*	53:47[c]
22	**2c**	**3c**	3	6	A	**4cc**	65	*Z* + *E*	45:55
23	**2c**	**3e**	5	5	B	**4ce**	64	*Z* + *E*	60:40
24	**2c**	**3f**	1	5	B	**4cf**	37	*Z* + *E*	63:37
25	**2c**	**3g**	1	7	B	**4cg**	81	*Z* + *E*	90:10
26	**2d**	**3a**	6	6.5	A	**4da**	41	–[d]	–
27	**2d**	**3b**	10	2	A	**4db**	90	*Z* + *E*	81:19
28	**2d**	**3c**	3	5.5	A	**4dc**	52	–[d]	–
29	**2d**	**3e**	5	5	B	**4de**	81	*Z* + *E*	80:20
30	**2d**	**3f**	1	7	B	**4df**	83	*Z* + *E*	86:14
31	**2d**	**3g**	1	5.5	A	**4dg**	80	Z	–
32	**2e**	**3a**	6	4	A	**4ea**	71	*Z* + *E*	32:68
33	**2e**	**3b**	10	2.5	A	**4eb**	64	*Z* + *E*	26:74
34	**2e**	**3c**	3	4.5	A	**4ec**	81	*Z* + *E*	24:76
35	**2e**	**3d**	5	4	C	**4ed**	46	*Z* + *E*	42:58[d]
36	**2e**	**3e**	5	5.5	B	**4ee**	32	*Z* + *E*	33:67
37	**2e**	**3e**	5	6.5	C	**4ee**	89	*Z* + *E*	33:67
38	**2e**	**3f**	1	3	C	**4ef**	59	*Z* + *E*	37:63[d]
39	**2e**	**3g**	1	3	A	**4eg**	53	*Z* + *E*	64:36[d]
40	**2e**	**3g**	1	3.5	C	**4eg**	19	*Z* + *E*	71:29[d]
41	**2f**	**3a**	6	5	A	**4fa**	81	*Z* + *E*	31:69[d]
42	**2f**	**3b**	10	2.5	A	**4fb**	90	*Z* + *E*	24:76
43	**2f**	**3c**	3	6	A	**4fc**	60	*Z* + *E*	27:73
44	**2f**	**3e**	5	5.5	B	**4fe**	40	*Z* + *E*	25:75
45	**2f**	**3e**	5	6.5	C	**4fe**	89	*Z* + *E*	88:12
46	**2f**	**3f**	1	2	C	**4ff**	79	*Z* + *E*	65:35
47	**2f**	**3g**	1	4	A	**4fg**	71	*Z* + *E*	23:77
48	**2g**	**3a**	6	2	A	**4ga**	82	*Z* + *E*	48:52
49	**2g**	**3b**	10	3	A	**4gb**	61	*Z* + *E*	48:52
50	**2g**	**3c**	1.5	5.5	A	**4gc**	82	*Z* + *E*	41:59
51	**2g**	**3e**	5	3	B	**4ge**	92	*Z* + *E*	52:48
52	**2g**	**3g**	1	7	A	**4gg**	92	*Z* + *E*	20:80
53	**2h**	**3b**	5	4	B	**4hb**	29	*Z* + *E*	66:34[d]
54	**2i**	**3a**	10	6	D	**4ia**[21]	36	*Z* + *E*	69:31
55	**2i**	**3b**	5	6.5	D	**4ib**[21]	40	*Z* + *E*	79:21
56	**2i**	**3b**	5	1.5	A	**4ib**[21]	51	*Z* + *E*	77:23
57	**2i**	**3c**	2	6	D	**4ic**	27	*Z* + *E*	79:21

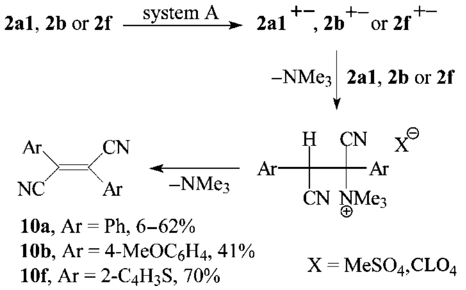
[a] System A: 50% aq. NaOH/CH_2Cl_2; system B: powdered K_2CO_3/CH_2Cl_2; system C: powdered K_2CO_3/CH_2Cl_2/DMSO; system D: powdered K_2CO_3/powdered NaOH/CH_2Cl_2. [b] Determined by NMR spectroscopy. [c] Determined by GC. [d] Stereochemistry not determined.

Equimolar amounts of **2a1** and **7a** gave crystalline product **9a** in 23% yield (Scheme 5). The key step of this reaction consists of cyclopropanation of the less sterically crowded γ,δ-double bond in diene **8aa** by **2a1**. Use of an excess of **2a1** (**2a1**/**7a** ≈ 2) did not increase the yield of **9a**, although intermediate diene **8aa**[29] could be prepared in yields of up to 92% from **7a** and **2a1** (molar ratio ≈ 15). Cyclopropane **9a** was prepared from salt **2a1** and isolated diene **8aa** in high yield (70%).



Scheme 5.

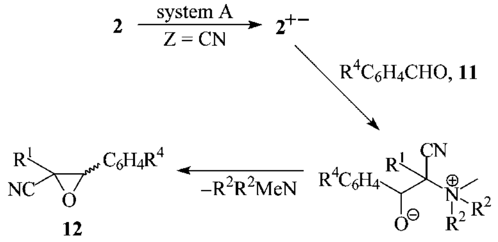
Attempted reactions of **2a1** with 2-(chloromethyl)thiophene (**7e**) and some other alkylating agents did not give the expected alkenes, but instead produced (*E*)-dicyanostilbene (**10a**).[34] Compound **10a** was also formed when **2a1** was stirred in system A without an alkylating agent, but its yield was observed to be dependent on the concentration of **2a1**. Thus, 6% yield was obtained in about 7 wt.-% solution in dichloromethane, while 62% yield was obtained when a 1.5 wt.-% solution was used. The formation mechanism of **10a** is not clear at the moment, but the alkylation–elimination sequence depicted in Scheme 6 seems plausible. This mechanism is analogous to that described for the synthesis of **10a** from chloro(phenyl)acetonitrile under PTC conditions.[34] Therefore preparation of alkenes (and dienes) is limited to active alkylating agents and only some ammonium salts.



Scheme 6.

Reaction of sulfur ylides with carbonyl compounds is a well-established method used for the synthesis of oxiranes.[35–38] Ylides of other elements (arsenic,[39–41] tellurium,[42,43] antimony,[44] selenium[45,46] and bismuth[47]) have also been applied for this purpose. The preparation of oxiranes substituted with EWGs is conveniently carried out by a Darzens condensation.[48,49]

Salt **2a1** reacted with aromatic aldehydes **11** in system A to give oxiranes **12** in moderate yields (Scheme 7, Table 3), but attempted extension of this reaction to other aldehydes, failed. Nevertheless, it has been demonstrated for the first time that ammonium salts react with some aromatic aldehydes in the presence of a base to give oxiranes **12**.



11	**a**	**b**	**c**	**d**	**e**
R^4	H	2-Cl	4-Cl	4-Me	4-F

Scheme 7.

The reactivity of the salts depends on the nature of the substituents present in the *para* position of phenyl ring. Thus, salt **2b**, which possesses an electron-donating methoxy group, reacts with all the above-mentioned electrophiles to give cyclopropanes **4ba**–**bc**,**be**–**bg** (Table 1), cyanoalkenes **8ba** and **8bd**[32] (Table 2), vinylcyclopropane **9b** (Scheme 5), oxiranes **12ba** and **12bc** (Table 3) and dicyanostilbene **10b**[52] (Scheme 6), usually in good yield. On the other hand, salt **2c**, which is substituted with an electron-withdrawing cyano group, reacts only with electrophilic alkenes to give the cyclopropanes **4ca**–**cc**,**ce**–**cg** in moderate yield (Table 1). The reactivity of salt **2b**, which is similar to that of **2a**, is due to the high electron density on the ylidic carbon atom.

Table 2. Synthesis of cyanoalkenes **8** in reactions of salts **2** with alkylating agents **7** in system A[a]

Entry	Salt	Alkylating agent	**7/2** [mol/mol]	Time [h]	Product	Yield	Isomer ratio[b]
1	**2a1**	**7a**	15	1.5	**8aa**[29]	75	87:13[c]
2	**2a1**	**7b**	5	3	**8ab**	94	–[d]
3	**2a1**	**7c**	1.25	7	**8ac**[30]	54	–[d]
4	**2a1**	**7d**	1	2	**8ad**[31]	80	–[d]
5	**2a2**	**7d**	1	5	**8ad**[31]	82	–[d]
6	**2a3**	**7a**	20	2.5	**8aa**[29]	77	85:15[e]
7	**2b**	**7a**	15	1.5	**8ba**	85	63:37[c]
8	**2b**	**7d**	1	2.5	**8bd**[32]	71	–[d]
9	**2g**	**7a**	10	1.5	**8ga**	75	78:22
10	**2g**	**7c**	1.25	7	**8gc**	71	70:30
11	**2g**	**7d**	1	4	**8gd**[33]	86	89:11
12	**2g**	**7e**	1	7.5	**8ge**	76	69:31

[a] 50% aq. NaOH/CH_2Cl_2. [b] Stereochemistry not determined. [c] Determined by ^1H NMR spectroscopy. [d] One isomer. [e] Determined by GC.

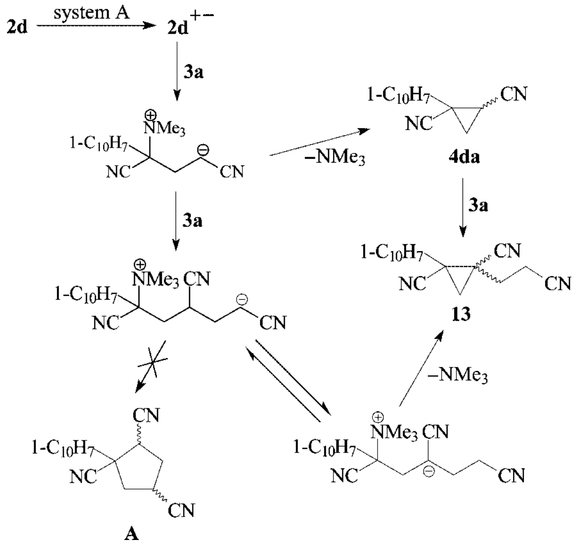
Table 3. Synthesis of oxiranes **12** in reactions of salts **2** with aldehydes **11** in system A[a]

Entry	Salt	Aldehyde	**11/2** [mol/mol]	Time [h]	Temperature [°C]	Product	Isomer	Yield [%]
1	**2a1**	**11a**	1	8	40	**12aa**[16]	*Z*	49
2	**2a1**	**11b**	1	9	40	**12ab**[50]	*Z*	48
3	**2a1**	**11c**	1	9	40	**12ac**[16]	*Z*	47
4	**2a1**	**11d**	0.5	8	40	**12ad**[51]	*Z*	46
5	**2a1**	**11e**	0.5	8	40	**12ae**	*Z*	45
6	**2b**	**11a**	1	15	40	**12ba**[16]	*Z*	35
7	**2b**	**11c**	1	10	40	**12bc**	*Z*	32
8	**2g**	**11a**	2	7	20–25	**12ga**	*Z* + *E*	52
9	**2g**	**11c**	1	10	20–25	**12gc**	*Z* + *E*	32

[a] 50% aq. NaOH/CH_2Cl_2.

Salts **2b**–**i** (Scheme 1) were allowed to react in basic two-phase systems with electrophilic alkenes **3** and/or alkylating agents **7** and/or aromatic aldehydes **11**. The results of these experiments are presented in Table 1, Table 2 and Table 3, respectively.

The reaction of salt **2d** with a large excess of **3a**, carried out in system A, produced, in addition to cyclopropane **4da**, the cyanoethyl derivative **13** (an isomeric tricyanocyclopentane structure **A** was excluded on the basis of APT measurements). The formation of **13** from isolated **4da** and **3a** (19% yield) does not explain how it is produced from **2d** and **3a**, because cyanoethylation of phenyl-substituted cyclopropane **4aa** essentially does not occur under the conditions of system A. Because of these observations, we suggest that formation of **13** occurs by deprotonation of the linear diadduct at γ-C, followed by its cyclization (Scheme 8).



Scheme 8.

The reaction of **2d** with **3a** or **3c** yielded one isomer of cyclopropanes **4da**,**dc** respectively, which was isolated by troublesome column chromatography and/or crystallization. Preparation of cyclopropanes **4db**,**dg** (in system A) and **4de**,**df** (in system B) was also successful. On the other hand, **2d** gave complex mixtures of products with **7a**,**c** or **11a** in system A.

Salts substituted with a 2-furyl (**2e**) or a 2-thienyl (**2f**) group reacted smoothly with **3** to give the corresponding cyclopropanes. Addition of DMSO to reaction mixtures containing powdered K_2CO_3 in dichloromethane (system C) increased the solubility of **2e**,**f** (and possibly **2e**,**f**$^{+-}$) to give the products in high yields. The reaction of **2f** with **3c** produced, in addition to (*Z*,*E*)-**4fc** (yield 60%), a small amount of dimer **10f**[53,54] (yield 19%), but in more concentrated systems these yields changed to 84% and 4%, respectively. Dimer **10f** was also produced when **2f** was allowed to react with methacrylonitrile (**5**) or crotononitrile, or when an electrophile was absent from system A. Formation of **10f** is reasonably explained by an alkylation–elimination route, as depicted in Scheme 6.

Of the two salts **2g**,**h** both of which have a substituted β,γ-double bond, only the first one gave satisfactory results when reacted with electrophiles **3**, **7** and **11**. Isolation of pure oxiranes **12** was rather troublesome due to both incomplete conversion of **11** and a Cannizzaro side-reaction. The use of TEBAC as a catalyst inhibits the PTC Cannizzaro reaction of benzaldehyde.[55] However, the use of this catalyst in the reaction of **2g** with **11a**,**c** carried out in system A, did not change the distribution of products.

Out of all the electrophilic alkenes that react with salt **2h**, only ester **3b** gave a mixture of (*Z*)- and (*E*)-**4hb** in low yield. Due to the many negative results with **2h**, its reactions with electrophiles **7** and **11** were not attempted.

Salt **2i**, which is substituted with an ester group, reacted with **3a**–**c** to give cyclopropanes **4ia**–**ic**[21] in 27–51% yield. Because **2i** is a weaker C-H acid than the cyano-substituted salt **2a1**, its reactions were usually carried out in the presence of a powdered mixture of NaOH and K_2CO_3 in dichloromethane (solid-liquid system D). Alkylation of **2i** with **7a** (in system A) or **7d** (in system D) did not occur or gave a mixture of products in low yields.

The stereochemistry of the majority of the cyclopropanes prepared was assigned on the basis of reported ^1H NMR spectroscopic data for (*Z*)-**4ab** and (*E*)-**4ab**,[21] and for some products was confirmed by NOE measurements. The stereochemistry of cyclopropanes (*Z*)-**4aa** and (*E*)-**4gg** was unequivocally confirmed by single-crystal X-ray analysis (Figure 1 and Figure 2, respectively).

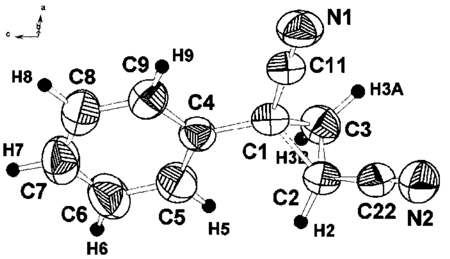


Figure 1. Crystal structure of cyclopropane (*Z*)-**4aa**

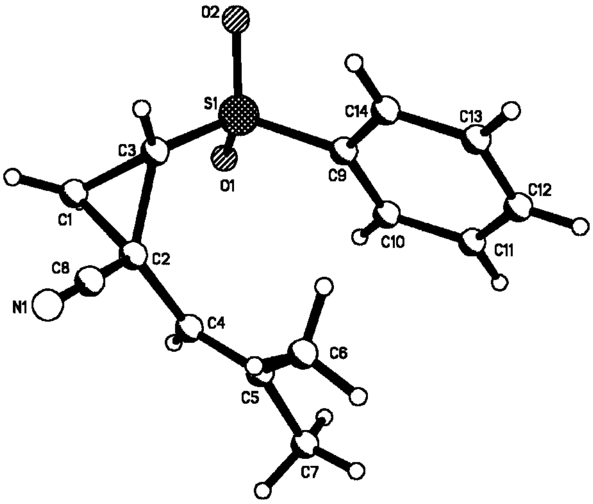


Figure 2. Crystal structure of cyclopropane (*E*)-**4gg**

Experimental Section

General Remarks: Melting (determined in a capillary tube apparatus) and boiling points are uncorrected. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ or [D$_6$]DMSO on a Varian Gemini 200, Varian Gemini 400 or Varian Gemini 500 spectrometer (at 200 MHz, 400 MHz and 500 MHz for ^{1}H and 50 MHz, 100 MHz and 125 MHz for ^{13}C respectively). Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) are given in hertz. GC analyses were performed with a Hewlett–Packard 5890 ser. II chromatograph, equipped with an HP50+ capillary column. Elemental analyses were performed with a Perkin–Elmer CHNO/S Ser. II 2400 microanalyser. HR-MS analyses were performed with an AMD 604 spectrograph. Column chromatography was carried out with Merck Kieselgel 60 (230–400 mesh) with a hexane/EtOAc (gradient) mixture as eluent. All solvents used were commercially available; Me_2SO_4 was purified before use.[56]

Synthesis of Aminonitriles 1a–h and Aminoester 1i: Aminonitriles **1a1**,[57]**1a2**,[57,58]**1a3**,[57,59]**1b**,[60]**1d**,[61]**1e**,[62,63]**1f**,[57,58]**1h**,[64] and aminoester **1i**[65] were synthesized according to literature methods.

1-(4-Cyanophenyl)-1-(dimethylamino)acetonitrile (1c): 4-Cyanobenzaldehyde (6.56 g, 0.055 mol) was addedto a mechanically stirred solution of $Na_2S_2O_5$ (10.46 g, 0.055 mol) in H_2O (35 mL). After 0.5 h a 40% aq. solution of dimethylamine (6.20 g, 7.0 mL, 0.055 mol) was added dropwise. The mixture was stirred for 0.5 h, cooled to 0 °C, and a solution of NaCN (2.70 g, 0.055 mol) in H_2O (10 mL) was added dropwise maintaining the temperature at 0 °C. Stirring was continued for 19 h, then the mixture was dissolved in H_2O (90 mL), extracted with CH_2Cl_2 (3 × 35 mL), and the combined organic extracts were washed with water (3 × 40 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue was used without further purification.

2-(Dimethylamino)-4-methylpent-3-enenitrile (1g): A solution of KCN (9.8 g, 0.15 mol) in H_2O (15 mL) was added dropwise over 1 h to a magnetically stirred solution of 3-methyl-2-butenal (8.4 g, 9.6 mL, 0.1 mol) and dimethylamine hydrochloride (12.2 g, 0.15 mol) in acetonitrile (40 mL) at –10 °C maintaining the temperature below –5 °C. Stirring was continued for 20 h. The mixture was dissolved in H_2O (200 mL), extracted with Et_2O (4 × 30 mL), and the combined organic extracts were washed with water (4 × 30 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue was purified by distillation under reduced pressure.

Synthesis of Salts 2: Me_2SO_4 [**1a1**,**1b**,**1c**,**1d**,**1g**/Me_2SO_4 (mol/mol) = 1.2; **1a2**,**1a3**,**1e**,**1f**/Me_2SO_4 (mol/mol) = 1.5; **1h**/Me_2SO_4 (mol/mol) = 1.8; **1i**/Me_2SO_4 (mol/mol) = 2.0] was added to a solution of aminonitrile **1a**–**h** or aminoester **1i** (0.03 mol) in CH_2Cl_2 (50 mL) at 0 °C. The mixture was left without stirring at 0 °C for 2 h and then at 20–25 °C for 24 h. The solvent was then evaporated and the residue was left for a further 48 h. If the residue solidified (**1a1**, **1a3**, **1b**–**d**, **1g**,**h**), acetone (10–25 mL) was added, and the crystals were filtered off, washed with acetone (4 × 5–10 mL) and dried under vacuum. If an oil was obtained (**1a2, 1e**,**f**, **1i**), it was dissolved in H_2O (20–50 mL), extracted with CH_2Cl_2 (3 × 10–15 mL), and the water phase was treated with 60% aq. $HClO_4$ (5.4 g, 3.4 mL, 0.032 mol). The resultant precipitate was filtered, washed with water (6–8 × 10–15 mL), then with diethyl ether (3–4 × 5–10 mL) and dried.

Synthesis of Cyclopropanes 4

Conditions A (50% aq. NaOH/CH_2Cl_2): 50% aq. NaOH (7.5 mL) was added dropwise to a vigorously stirred solution of salt **2** (3 mmol) and electrophilic alkene **3** (amount given in Table 1) in CH_2Cl_2 (45 mL). The stirring was continued for the time given in Table 1, the mixture was diluted with water (100 mL), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL), and the combined organic extracts were washed with water (3 × 40 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel, and the crude products were further purified by Kugelrohr distillation, crystallisation or by column chromatography (Table 1).

Conditions B (K_2CO_3/CH_2Cl_2): Powdered K_2CO_3 (30 mmol, 4.15 g) was added to a vigorously stirred solution of salt **2** (3 mmol) and electrophilic alkene **3** (amount given in Table 1) in CH_2Cl_2 (45 mL). Stirring was continued for the time given in Table 1, then the mixture was diluted with water (100 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were washed with water (3 × 40 mL) [in the case of reactions with salts **2a2** and **2a3** the combined organic extracts were first washed with 3% aq. HCl (2 × 30 mL)], dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel, and the crude products were further purified by Kugelrohr distillation, crystallisation or by column chromatography (Table 1).

Conditions C (K_2CO_3/CH_2Cl_2/DMSO): Powdered K_2CO_3 (30 mmol, 4.15 g) was added to a vigorously stirred solution of salt

2 (3 mmol) and electrophilic alkene **3** (amount given in Table 1) in CH_2Cl_2 (40 mL) and DMSO (12 mL). Stirring was continued for the time given in Table 1. The mixture was then diluted with water (100 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were washed with water (4 × 40 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel, and the crude products were further purified by Kugelrohr distillation, crystallisation or by column chromatography (Table 1).

Conditions D ($NaOH/K_2CO_3/CH_2Cl_2$): Powdered NaOH (30 mmol, 1.2 g) and powdered K_2CO_3 (15 mmol, 2.1 g) were added to a vigorously stirred solution of salt **2** (3 mmol) and electrophilic alkene **3** (amount given in Table 1) in CH_2Cl_2 (45 mL). Stirring was continued for the time given in Table 1. Work-up and purification were as described for conditions A.

Synthesis of 1-Methyl-2-phenylcyclopropane-1,2-dicarbonitrile (6): 50% aq. NaOH (10 mL) was added dropwise to a vigorously stirred solution of salt **2a1** (5 mmol, 1.43 g) and methacrylonitrile (**5**; 25 mmol, 1.68 g, 2.1 mL) in CH_2Cl_2 (50 mL). Stirring was continued for 7.5 h, then the mixture was diluted with water (100 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were washed with water (3 × 40 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel, and the crude product was further purified by column chromatography and crystallization.

Synthesis of Alkenes 8: 50% aq. NaOH (5 mL) was added dropwise to a vigorously stirred solution of salt **2** (3 mmol) and alkylating agent **7** (amount given in Table 2) in CH_2Cl_2 (15 mL). Stirring was continued for the time given in Table 2, then the mixture was diluted with water (50 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel and the crude products were further purified by Kugelrohr distillation, crystallization or by column chromatography (Table 2).

Synthesis of 2-(2-Cyano-2-phenylethenyl)-1-phenylcyclopropanecarbonitrile (9a) and 2-[2-Cyano-2-(4-methoxyphenyl)ethenyl]-1-(4-methoxyphenyl)cyclopropanecarbonitrile (9b): 50% aq. NaOH (6 mL) was added dropwise to a vigorously stirred solution of salt **2a1** or **2b** (4.5 mmol) and cyanodiene **8aa** or **8ab** (4.5 mmol) in CH_2Cl_2 (15 mL). Stirring was continued for 2 h, then the mixture was diluted with water (50 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel and the products were purified by column chromatography and crystallized.

Synthesis of 2,3-Diarylbut-2-enedinitriles 10a, 10b and 10f: 50% aq. NaOH (20 mL) was added dropwise to a vigorously stirred solution of salt **2a1**, **2b** or **2f** (7 mmol) in CH_2Cl_2 (100 mL). Stirring was continued for 6 h, then the mixture was diluted with water (100 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with water (3 × 50 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel and the crude products were crystallised.

Synthesis of Oxiranes 12: 50% aq. NaOH (10 mL) was added dropwise to a vigorously stirred solution of salt **2** (7 mmol) and aldehyde **11** (amount given in Table 3) in CH_2Cl_2 (40 mL). Stirring was continued at the temperature and for the time given in Table 3, then the mixture was diluted with water (80 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with water (3 × 30 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel and the crude products were purified by Kugelrohr distillation, crystallisation or by column chromatography (Table 3).

Synthesis of 1-(2-Cyanoethyl)-2-naphthalen-1-ylcyclopropane-1,2-dicarbonitrile (13): 50% aq. NaOH (7.5 mL) was added dropwise to a vigorously stirred solution of salt **2d** (3 mmol, 1.0 g) and acrylonitrile (**3a**; 30 mmol, 1.6 g, 2.0 mL) in CH_2Cl_2 (15 mL). Stirring was continued for 7 h, ten the mixture was diluted with water (50 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with water (4 × 25 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was passed through a short pad of silica gel and the crude product was further purified by column chromatography.

X-ray Crystallographic Study: Data collection for (*Z*)-**4aa** was performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-K_α radiation (Table 4). The crystal was positioned at 65 mm from the KM4CCD camera. 748 Frames were measured at 1.6° intervals with a counting time of 10 s. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction programs (Wrocław). The structure was solved by direct methods[66] and refined by using SHELXL.[67] The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted *R* factors (*wR*) and all goodness-of-fit *S* values are based on F^2. Conventional *R* factors are based on *F*, with *F* set to zero for negative F^2. The $F_o^2 > 2\sigma(F_o^2)$ criterion was used only for calculating *R* factors and is not relevant to the choice of reflections for the refinement. The *R* factors based on F^2 are about twice as large as those based on *F*. All hydrogen atoms were located from a differential map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in ref.[68]

Data collection for (*E*)-**4gg** was carried out using a KUMA KM-4 diffractometer with graphite-monochromated Mo-K_α radiation (Table 4). The data were collected at room temperature using the ω-2θ scan technique. The intensity of the control reflections varied by less than 5%, and a linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects, but no absorption correction was applied. The structure was solved by direct methods[66] and refined by full-matrix least-squares techniques (SHELXL).[67] The non-hydrogen atoms were refined anisotropically, whereas the H-atoms were placed in the calculated positions and their thermal parameters were refined isotropically. The atomic scattering factors were taken from the International Tables of Crystallography.[69]

CCDC-198409 [for (*E*)-**4gg**] and CCDC-198410 [for (*Z*)-**4aa**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: Yields, physical and spectral properties, elemental analyses or HRMS of aminonitriles **1c**,**g**, salts **2**, cyclopropanes **4**, **6**, **9** and **13**, alkenes **8**, dimers **10** and oxiranes **12**. Investigation of the stereochemistry of cyclopropanes **4** and oxiranes **12** is also described (see also the footnote on the first page of this article).

Table 4. Summary of data collection, structure solution and refinement details for (*E*)-**4gg** and (*Z*)-**4aa**

	(*E*)-4gg	**(*Z*)-4aa**
Empirical formula	$C_{14}H_{15}NO_2S$	$C_{11}H_{20}N_2$
Formula mass	261.33	180.29
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
a [Å], α [°]	30.319(6), 90	6.4370(13), 90
b [Å], β [°]	5.9330(10), 96.28(3)	8.5400(17), 95.82(3)
c [Å], γ [°]	14.940(3), 90	16.630(3), 90
Volume [Å^3]	2671.3(9)	909.5(3)
Z	8	4
Density (calculated)	1.300 mg/m^3	1.317 mg/m^3
Absorption coefficient	0.236 mm^{-1}	0.078 mm^{-1}
F(000)	1104	400
Crystal size	0.3 × 0.3 × 0.28 mm	0.7 × 0.7 × 0.23 mm
θ range for data collection	1.35 to 30.08	3.43 to 25.00
Index ranges	$-30 \le h \le 0$, $0 \le k \le 8$, $-16 \le l \le 16$	$-7 \le h \le 7$, $-10 \le k \le 10$, $-19 \le l \le 19$
Reflections collected	3265	13502
Independent reflections	3205 [R(int) = 0.0588]	1607 [R(int) = 0.0634]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3198/0/178	1607/0/151
Goodness-of-fit on F^2	1.026	1.142
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0587$, $wR_2 = 0.1620$	$R_1 = 0.0600$, $wR_2 = 0.1740$
R indices (all data)	$R_1 = 0.0887$, $wR_2 = 0.2017$	$R_1 = 0.0786$, $wR_2 = 0.1982$
Largest diff. peak and hole	0.540 and –0.314 e Å^3	0.251 and –0.164 e Å^3

Acknowledgments

The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Lab. at the Chemistry Department of the University of Warsaw.

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[1] A. W. Zugravescu, M. Petrovanu, in *N-Ylide Chemistry*, McGraw-Hill, New York, **1976**, p. 1–314.
[2] S. H. Pine, *Org. React.* **1970**, *18*, 403–464.
[3] S. S. Bhattacharjee, H. Ila, H. Junjappa, *Synthesis* **1982**, 301–303.
[4] A. M. Shestopalov, V. P. Litvinov, L. A. Rodinovskaya, Y. A. Sharanin, *Zh. Org. Khim.* **1991**, *27*, 146–155.
[5] N. H. Vo, C. J. Eyermann, C. N. Hodge, *Tetrahedron Lett.* **1997**, *38*, 7951–7954.
[6] L. M. Harwood, R. J. Vickers, in *The Chemistry of Heterocyclic Compounds* (Eds.: E. C. Taylor, P. Wipf), vol. 59 (Eds.: A. Padwa, W. H. Pearson), Wiley, New York, **2002**, p. 169–252; Y. Terao, M. Aono, K. Achiwa, *Heterocycles* **1988**, *27*, 981–1008.
[7] C. D. Papageorgiou, S. V. Ley, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2003**, *42*, 828–831.
[8] A. Jończyk, A. Kowalkowska, *Synthesis* **2002**, 674–680.
[9] A. Jończyk, A. Konarska, *Synlett* **1999**, 1085–1087.
[10] E. V. Dehmlow, S. S. Dehmlow, *Phase-Transfer Catalysis*, 3rd ed., Verlag Chemie, Weinheim, **1993**, p. 1–499.
[11] C. M. Starks, C. L. Liotta, M. Halpern, *Phase-transfer Catalysis*, Chapman & Hall, New York, London, **1994**, p. 1–668.
[12] M. Mąkosza, M. Fedoryński, *Polish J. Chem.* **1996**, *70*, 1093–1110.
[13] M. Mąkosza, M. Fedoryński, in *Interfacial Catalysis* (Ed.: A. G. Volkov), Marcel Dekker, Inc., New York, **2003**, p. 159–201.
[14] M. Makosza, B. Serafinowa, T. Bolesławska, *Roczniki Chem.* **1968**, *42*, 817–822.
[15] M. Schlosser, in *Struktur und Reaktivität polarer Organometalle*, Springer-Verlag, Berlin, Heidelberg, New York, **1973**, p. 88.
[16] M. Mąkosza, A. Kwast, E. Kwast, A. Jończyk, *J. Org. Chem.* **1985**, *50*, 3722–3727.
[17] R. Yoneda, K. Santo, S. Hurasawa, T. Kurihara, *Synth. Commun.* **1987**, *17*, 921–927.
[18] A. Jończyk, A. Kwast, M. Mąkosza, *Tetrahedron Lett.* **1979**, *20*, 541–544.
[19] S. D. Clarke, C. R. Harrison, P. Hodge, *Tetrahedron Lett.* **1980**, *21*, 1375–1378.
[20] T. Saegusa, K. Yonezawa, I. Murase, T. Konoike, S. Tomita, Y. Ito, *J. Org. Chem.* **1973**, *38*, 2319–2328.
[21] C. Chen, Y. Liao, Y. Z. Huang, *Tetrahedron* **1989**, *45*, 3011–3020.
[22] T. Kurihara, K. Santo, S. Harusawa, R. Yoneda, *Chem. Pharm. Bull.* **1987**, *35*, 4777–4788.
[23] See page 108 in: H. A. Bruson, *Org. React.* **1949**, *5*, 79–135.
[24] G. Jones, *Org. React.* **1967**, *15*, 204–599.
[25] A. Maercker, *Org. React.* **1965**, *14*, 270–490.
[26] B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863–927.
[27] L. Alcaraz, J. J. Harnett, C. Mioskowski, J. P. Martel, T. Le Gall, D. S. Shin, J. R. Falck, *Tetrahedron Lett.* **1994**, *35*, 5453–5456.
[28] A. Seyer, L. Alcaraz, C. Mioskowski, *Tetrahedron Lett.* **1997**, *38*, 7871–7874.
[29] S. Hughes, C. J. M. Stirling, *J. Chem. Soc., Chem. Commun.* **1982**, 237–238.
[30] B. H. Baretz, A. K. Singh, R. S. H. Liu, *Nouv. J. Chim.* **1981**, *5*, 297–303.
[31] S. Wawzonek, E. M. Smolin, *Org. Synth., Coll. Vol.* **1955**, *III*, 715–717.
[32] B. Zupančič, M. Kokalj, *Synthesis* **1981**, 913–915.
[33] T. Janecki, *Synthesis* **1991**, 167–168.
[34] M. Mąkosza, B. Serafinowa, I. Gajos, *Roczniki Chem.* **1969**, *43*, 671–676.
[35] B. M. Trost, L. S. Melvin, in *Sulfur Ylides: Emerging Synthetic Intermediates*, Academic Press, **1975**, p. 37–76.
[36] J. Aubé, in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost and I. Fleming), vol. 1 (Ed.. S. L. Schreiber), Pergamon Press, Oxford, **1991**, p. 819–825.
[37] C. R. Johnson, in *Comprehensive Organic Chemistry* (Eds.: D. Barton, W. D. Ollis), vol. 3 (Ed.: D. Neville Jones), Pergamon Press, **1979**, p. 252–254.

[38] Y. G. Gololobov, A. N. Nesmeyanow, V. P. Lysenko, I. E. Boldeskul, *Tetrahedron* **1987**, *43*, 2609–2651.
[39] D. Lloyd, I. Gosney, R. A. Ormiston, *Chem. Soc. Rev.* **1987**, *16*, 45–74.
[40] J. B. Ousset, C. Mioskowski, G. Solladie, *Tetrahedron Lett.* **1983**, *24*, 4419–4422.
[41] L. Shi, W. Wang, Y. Z. Huang, *Tetrahedron Lett.* **1988**, *29*, 5295–5296.
[42] L. L. Shi, Z. L. Zhou, Y. Z. Huang, *Tetrahedron Lett.* **1990**, *31*, 4173–4174.
[43] A. Osuka, H. Suzuki, *Tetrahedron Lett.* **1983**, *24*, 5109–5112.
[44] Y. Z. Huang, Y. Liao, C. Chen, *J. Chem. Soc., Chem. Commun.* **1990**, 85–86.
[45] D. Van Ende, A. Krief, *Tetrahedron Lett.* **1976**, *17*, 457–460.
[46] See page 1114 in: D. L. J. Clive, *Tetrahedron* **1978**, *34*, 1049–1132.
[47] Y. Matano, *J. Chem. Soc., Perkin Trans. 1* **1994**, 2703–2709.
[48] M. Ballester, *Chem. Rev.* **1955**, *55*, 283–300.
[49] M. S. Newman, B. J. Magerlein, *Org. React.* **1949**, *5*, 413–440.
[50] G. Kyriakakou, J. Seyden-Penne, *Tetrahedron Lett.* **1974**, *15*, 1737–1740.
[51] N. McDonald, D. G. Hill, *J. Org. Chem.* **1970**, *35*, 2942–2948.
[52] P. S. Lianis, N. A. Rodios., N. E. Alexandrou, *Liebigs Ann. Chem.* **1987**, 537–540.
[53] H. M. Refat, J. Waggenspack, M. Dutt, H. Zhang, A. A. Fadda, E. Biehl, *J. Org. Chem.* **1995**, *60*, 1985–1989.
[54] H. M. Refat, A. A. Faddo, E. Biehl, *J. Fluorine Chem.* **1996**, *76*, 99–103.
[55] G. W. Gokel, H. M. Gerdes, N. W. Rebert, *Tetrahedron Lett.* **1976**, *17*, 653–656.
[56] A. I. Vogel, in *Preparatyka Organiczna*, 2nd ed., WNT, Warszawa, **1984**, p. 239.
[57] H. M. Taylor, C. M. Hauser, *Org. Synth., Coll. Vol.* **1973**, *V*, 437–439.
[58] K. Takahashi, M. Matsuzaki, K. Ogura, H. Iida, *J. Org. Chem.* **1983**, *48*, 1909–1912.
[59] D. J. Bennett, G. W. Kirby, V. A. Moss, *J. Chem. Soc. C* **1970**, 2049–2051.
[60] G. F. Morris, C. R. Hauser, *J. Org. Chem.* **1961**, *26*, 4741–4743.
[61] T. van Es, W. Prinz, *J. Chem. Soc.* **1964**, 5493–5494.
[62] S. F. Dyke, E. P. Tiley, A. W. C. White, D. P. Gale, *Tetrahedron* **1975**, *31*, 1219–1222.
[63] H. Bredereck, G. Simchen, W. Kantlehner, *Chem. Ber.* **1971**, *104*, 932–940.
[64] K. Shakhidayatov, L. A. Yanowskaya, V. F. Kucherov, *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1969**, 953–955.
[65] G. Brancaccio, A. Larizza, *Gazz. Chim. Ital.* **1964**, *94*, 37–47.
[66] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[67] G. M. Sheldrick, *SHELXL93.Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
[68] *International Tables for Crystallography* (Ed.: A. J. C. Wilson), Kluwer, Dordrecht, vol. C, **1992**.
[69] *International Tables for Crystallography*, Kynoch Press, Birmingham, **1974**, vol. IV.

Received: August 5, 2004