mixed with ice. The aqueous phase was extracted with dichloromethane, and the organic layer was washed with water until neutrality. After evaporation of the solvent, the organic residue was chromatographed with hexane/ether, 60/40, as the eluent. Yield: 0.31 g (ca. 50%) of a yellow solid, which was recrystallized in CH_2Cl_2/hexane. ^{31}P NMR (CH_2Cl_2): δ +24.0 ppm, $^{1}J(^{31}P\text{-}^{183}W)$ = 224.6 Hz. ^{1}H NMR ($CDCl_3$): δ 2.31 (s broad, 3 H, Me), 2.40 (s broad, 3 H, Me), 6.64 (d, ^{2}J(H–P) = 37.3 Hz, 1 H, =CH-P), 6.87 (d, ^{3}J(H–H) = 4 Hz, 1 H, Hβ thiophene), 7.43–7.58 (m, 5 H, Ph), 7.59 (d, ^{3}J(H–H) = 4 Hz, 1 H, Hβ' thiophene), 9.81 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ 15.53 (d, ^{3}J(C–P) = 8 Hz, Me), 17.92 (d, ^{3}J(C–P) = 10.5 Hz, Me), 182.58 (s, CHO), 195.66 (d, ^{2}J(C–P) = 6.5 Hz, cis CO), 197.72 (d, ^{2}J(C–P) = 20 Hz, trans CO). Mass spectrum (^{184}W): m/z 622 (M^+, 19), 481 ($M^+ - 5CO - H$, 100). Anal. Calcd for $C_{22}H_{15}O_6PSW$: C, 42.44; H, 2.41. Found: C, 42.17; H, 2.48.

A New Version of the Peterson Olefination Using Bis(trimethylsilyl)methyl Derivatives and Fluoride Ion as Catalyst

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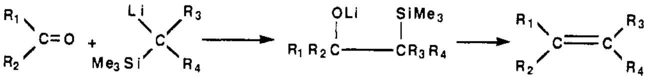
Reaction between a variety of bis(trimethylsilyl)methyl derivatives and carbonyl compounds under fluoride ion as catalyst is described. The reaction works especially well with nonenolizable carbonyl compounds to give the expected alkenes in high yields and, in some cases, with high stereoselectivity. Application of this methodology to an intramolecular alkenation providing a tricyclic benzocarbacephem ring system is also described.

The Peterson reaction[1] (eq 1) has proved to be one of the best methodologies for carbonyl olefination. Conceptually, it involves reaction between a carbonyl component **1** and an α-silyl carbanion **2**, followed by acidic or basic elimination of the resulting β-hydroxyalkylsilane **3**. This method is a powerful alternative to the Wittig olefination,[2] especially because the elimination step can be directed in either a syn or an anti manner[3] and, also, because a wider range of alkenes can be obtained from a wide variety of α-lithio silanes.[4] Recently, the use of fluoride ion as promoter of carbon nucleophiles from organosilicon compounds has become a field of considerable importance in organic synthesis.[5] Several groups have demonstrated that desilylation of organosilanes containing a C–SiR_3 bond by means of fluoride ion is an effective way for the transfer of carbanions to electrophilic centers.[6] However, very few examples have been described concerning the formation of α-silyl carbanions promoted by fluoride ion on organosilicon compounds involving two trialkylsilyl units in the same carbon atom.[7] Recently, we undertook a study on this subject, and found[8] that N-[bis(trimethylsilyl)-



1 2 3 4

(1)

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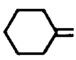
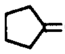
Table I. Fluoride Ion Catalyzed Reaction between Carbonyl Compounds and Bis(trimethylsilyl)methyl Derivatives 5–7[a]

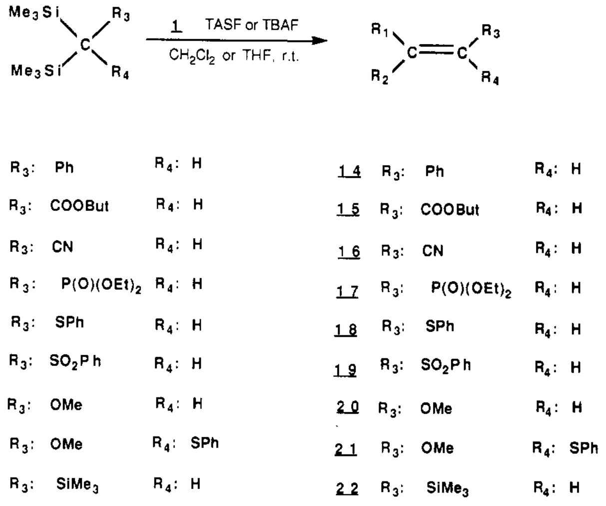
entry	carbonyl component	silyl component	solvent	*T*, °C	time, h	product[b]	yield,[c] %	*E*/*Z*[d]
a	C_6H_5CHO	**5**	CH_2Cl_2	20	1	**14**	92	50/50
		7	THF	20	1	**16**	90	50/50
			THF	−70	0.5	**16**	86	80/20
			CH_2Cl_2	−100	1	**16**	90	95/5
b	4-Cl-C_6H_4CHO	**5**	CH_2Cl_2	20	1	**14**	98	50/50
		6	THF	20	1	**15**	93	100/0
		7	THF	20	1	**16**	91	57/43
			CH_2Cl_2	−100	1	**16**	91	90/10
c	4-Me-C_6H_4CHO	**5**	CH_2Cl_2	20	1	**14**	82	50/50
		6	CH_2Cl_2	20	1	**15**	96	100/0
		7	THF	20	1	**16**	81	80/20
			THF	−78	0.5	**16**	–[e]	85/15
			CH_2Cl_2	−75	0.5	**16**	–[e]	85/15
			CH_2Cl_2	−100	0.5	**16**	87	97/3
d	4-MeO-C_6H_4CHO	**5**	CH_2Cl_2	20	1	**14**	76	50/50
		6	THF	20	0.5	**15**	78	100/0
		7	THF	20	0.5	**16**	80	62/38
			CH_2Cl_2	−75	0.5	**16**	76	88/12
			CH_2Cl_2	−100	0.5	**16**	75	96/4
e	$C_6H_5CH{=}CMeCHO$	**5**	CH_2Cl_2	20	1	**14**	87	70/30
		6	THF	20	1	**15**	90	100/0
		7	THF	20	1	**16**	72	100/0
f	Me_3CCHO	**5**	THF	70	1	**14**	50	100/0
		6	THF	20	2	**15**	78	100/0
		7	THF	20	1	**16**	88	100/0
a	$C_6H_5COC_6H_5$	**6**	THF	20	1	**15**	94	–
		7	THF	20	1	**16**	88	–
h	Me_3CCOMe	**7**	THF	20	1	**16**	25[f]	100/0
i	C_6H_5COMe	**7**	THF	20	1	**16**	40[g]	100/0
i	Me_2CHCHO	**7**	THF	20	1	**16**	65[h]	100/0
k		**6**	THF	20	1	–[i]	–	–
		7	THF	20	1	**16**	71[j]	–
l		**7**	THF	20	0.5	**16**	80[j]	–

[a] All reactions were conducted on a 3-mmol scale, following the typical procedure described in the Experimental Section. [b] All products were fully characterized by physical and spectroscopic data. [c] Yields refer to isolated materials. [d] The *E*/*Z* ratio was determined by 300-MHz ^1H NMR spectroscopy of the crude reaction mixture. [e] Not isolated. [f] 87% trimethylsilyl enol ether isolated. [g] 50% trimethylsilyl enol ether isolated. [h] 10% of the trimethylsilyl enol ether was formed. [i] No reaction. [j] No trimethylsilyl enol ether detected in the reaction crude.

methyl]imines and related compounds easily undergo olefination under fluoride ion catalysis. Consequently, we thought that this methodology could be used to prepare a wider range of alkenes, starting from a variety of bis(trimethylsilyl)methyl derivatives. We report here the first additional examples of this new version of the Peterson olefination that demonstrate its potential usefulness in Organic Chemistry.

To test our intended methodology (Scheme I), compounds **5**–**13** were prepared according with literature precedents[9] and reacted with a variety of selected carbonyl compounds in the presence of tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF).[10,11] Reaction of α,α-bis(trimethylsilyl)toluene (**5**) with benzaldehyde under nucleophilic catalysis[9a] with a catalytic amount of TASF in methylene chloride solution at room temperature cleanly afforded stilbene in 92% isolated yield. Generally, the reactions were carried out either in methylene chloride or tetrahydrofuran at room temperature or under reflux conditions. The reaction has been performed on a variety of structurally different carbonyl compounds to determine the scope and limitations of this method. Some results of this study are summarized in Table I, to illustrate the efficiency and the applicability of the method. As shown in the table, the reaction was

Scheme I



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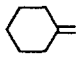
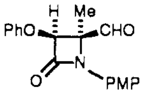
(11) The olefination reaction also worked well when tetrabutylammonium fluoride (TBAF) was used as the initiator. For the use of various fluoride ion sources in Organic Chemistry, see: Clark, J. H. *Chem. Rev.* **1980**, *80*, 429.

Table II. Fluoride Ion Catalyzed Reaction between Carbonyl Compounds and Bis(trimethylsilyl)methyl Derivatives 8–13[a]

entry	carbonyl component	silyl component	T, °C	time, h	product[b]	yield,[c] %	E/Z[d]
a	C_6H_5CHO	**8**	20	1	**17**	60	84/16
		12	20	1	**21**	92	50/50
		13	70	1	**22**	94	72/28
b	4-Cl-C_6H_4CHO	**8**	20	1	**17**	70	83/17
		9	0	1	**18**	94	50/50
c	4-NC-C_6H_4CHO	**10**	20	1	**19**	70	100/0
d	4-Me-C_6H_4CHO	**8**	20	1	**17**	65	85/15
		9	0	1	**18**	92	50/50
		10	0	1	**19**	86	100/0
e	4-MeO-C_6H_4CHO	**8**	20	1	**17**	60	86/14
		13	20	2	**22**	94	73/37
f	$C_6H_5CH{=}CHCHO$	**9**	0	1	**18**	86	100/0
g	$C_6H_5CH{=}CMeCHO$	**9**	20	1	**18**	96	50/50
		12	20	1	**21**	95	100/0
		13	70	2	**22**	92	70/30
h	Me_3CCHO	**8**	70	1	**17**	62	50/50
i	$C_6H_5COC_6H_5$	**9**	0	1	**18**	89	–
		10	20	1	**19**	72	–
j	C_6H_5COMe	**9**	20	1	**18**	62	50/50
		10			**19**	70	100/0
k		**9**	20	1	**18**	43	–
		10	20	1	**19**	70	–
l		**9**	20	2	**18**	58	50/50

[a] All reactions were carried out in tetrahydrofuran on a 3-mmol scale, following the procedure described in the Experimental Section. [b] All products were fully characterized by physical and spectroscopic data. [c] Yields refer to isolated materials. [d] The E/Z ratio was determined by 300-MHz ^1H NMR spectroscopy of the crude reaction mixture. PMP: 4-methoxyphenyl group.

exceptionally effective for nonenolizable carbonyl compounds, giving a variety of alkenes in excellent yields. With enolizable aldehydes or ketones the alkene was obtained, accompanied with the corresponding trimethylsilyl enol ether, depending on the compound used. For example, reaction between cyclohexanone and *tert*-butyl bis(trimethylsilyl)acetate (**6**) gave only 1-(trimethylsiloxy)cyclohexene, whereas bis(trimethylsilyl)acetonitrile (**7**) gave the desired alkenenitrile in 71% isolated yield, without formation of trimethylsilyl enol ether of cyclohexanone. With α,β-unsaturated aldehydes only 1,2-addition took place and the expected functionalized diene was produced generally in high yield. In the case of pinacolone the reaction was sluggish, probably by steric factors, and 1-*tert*-butyl-1-(trimethylsiloxy)ethene was the predominant product obtained.

In order to determine the scope of the method, we next examined the behavior of some bis(trimethylsilyl)methyl heterocompounds in this Peterson type reaction. For example, reaction between *O,O*-diethyl [bis(trimethylsilyl)methyl]phosphonate (**8**) and nonenolizable carbonyl compounds under TASF catalysis gave a mixture of the corresponding cis and trans isomers of **17** in good yields. Vinyl sulfides **18**,[12] an important class of masked reagents for umpolung reactivity,[13] could also be obtained under mild conditions by using bis(trimethylsilyl)(phenylthio)methane (**9**) as source of α-(trimethylsilyl)(phenylthio)methyl carbanion.[14] As shown in Table II, the reaction between **9** and carbonyl compounds in the presence of either TBAF or TASF as catalyst works especially well with nonenolizable carbonyl compounds to give vinyl sulfides **18** in excellent yields as equimolar mixtures of the corresponding trans and cis isomers. With enolizable ketones, as expected by Seebach results,[15] the corresponding vinyl sulfide was produced in lower yield, together with the corresponding trimethylsilyl enol ether as main product. In contrast, under similar conditions, bis(trimethylsilyl)(phenylsulfonyl)methane (**10**) afforded vinylic sulfones **19**[16] without formation of trimethylsilyl enol ethers. Surprisingly, in the case of bis(trimethylsilyl)methoxymethane (**12**) we did not observe any formation of the vinyl ether **20**.[17] However, when the reaction was examined for bis(trimethylsilyl)methoxy(phenylthio)methane (**12**), the expected ketene *O,S*-acetal **21** was obtained in excellent yield.[18] Under nucleophilic conditions, tris(trimethylsilyl)methane (**13**)[19] also produced the expected α-silyl carbanion. Reaction between **13** and nonenolizable carbonyl compounds in the presence of TASF catalyst in refluxing THF and further aqueous workup afforded vinyl silanes in high chemical yields.[20] As can be seen from the results reported, the reaction with enolizable aldehydes and ketones generally follows a different course. With the exceptions described above, the carbanionic species generated from those bis(trimethylsilyl)methyl reagents and fluoride ion acted as a base rather than as a nucleophile. The use of higher reaction temperatures, or the change of the solvent (i.e. CH_3CN or HMPA), did not modify the reaction course, and the

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[13] For reviews, see: (a) Grobel, B. T.; Seebach, D. *Synthesis* **1977**, 357. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239. (c) *Umpoled Synthons*; Hase, T. A., Ed.; John Wiley: New York, 1987.

[14] For a recent review on organosulfur–silicon compounds, see: Block, E.; Aslam, M. *Tetrahedron* **1988**, *44*, 281.

[15] Grobel, B. T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.

[16] For a review on vinylic sulfones, see: Durst, T. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, p 197.

[17] Vinyl ethers from (trimethylsilyl)methoxymethane, see ref 9 and Kende, A. S.; Blacklock, T. J. *Tetrahedron Lett.* **1980**, *21*, 3119. Magnus, P.; Roy, G. *J. Chem. Soc., Chem. Commun.* **1979**, 822.

[18] Ketene-O,S-acetals from (trimethylsilyl)methoxy(phenylthio)methane: Hackett, S.; Livinghouse, T. *Tetrahedron Lett.* **1982**, *23*, 3265 and ref 9h.

[19] Sakurai, H.; Nishiwaki, K.; Kira, M. *Tetrahedron Lett.* **1973**, 4193.

[20] Trimethylchlorosilane addition to the hot reaction mixture must be avoided, since in such a case, protodesilylation takes place to give the corresponding alkene instead of the expected vinylsilane.

Table III. Peterson-Type Alkenations under Alkoxide Catalysis[a]

carbonyl component	silyl component	catalyst	time, h	product[b]	yield,[c] %	E/Z[d]
4-Me-C_6H_4CHO	**7**	NaOMe	6	**16**	77	16/84
		KO^{t}Bu	0.5	**16**	68	66/34
4-MeOOC-C_6H_4CHO	**10**	NaOMe	0.5	**19**	67	100/0

[a] All reactions were carried out in tetrahydrofuran at room temperature in a 3-mmol scale: carbonyl component:silyl component:catalyst (1:2.5:0.1). [b] Products were characterized by physical and spectroscopic data. [c] Yields refer to isolated materials by Kügelrohr distillation. [c] E/Z ratio determined by 300-MHz ^{1}H NMR spectroscopy of the crude reaction mixture.

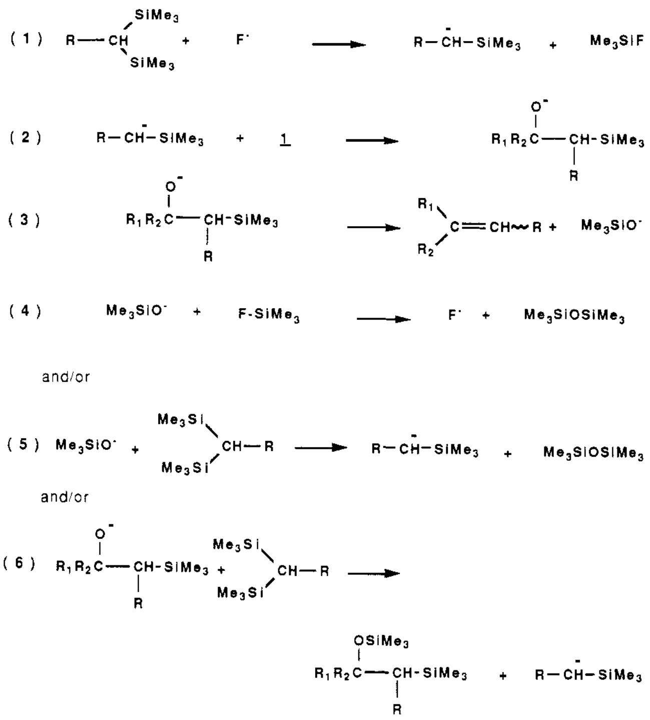
corresponding trimethylsilyl enol ethers were the main products obtained.

Concerning the stereoselectivity of the reaction, generally a mixture of cis and trans isomers was produced in nearly equal amounts. As shown in Table I, reaction between *tert*-butyl bis(trimethylsilyl)acetate (**6**) and nonenolizable carbonyl comounds only furnished the corresponding *trans*-alkene **15**.[21] When the reaction was tested for bis(trimethylsilyl)acetonitrile (**7**) and aromatic aldehydes, the composition product seems to be strongly dependent on the reaction conditions used, and the best results for a high stereoselectivity were obtained when the fluoride ion mediated alkenation was performed in methylene chloride at −100 °C; under these conditions, the corresponding *trans*-**16**[22] was produced as main product. Particularly noteworthy is also the fact that the reaction between **10** and carbonyl compounds under TASF catalysis only produced trans isomers of **19**, which contrasts with the lack of stereoselectivity using (phenylsulfonyl)(trimethylsilyl)methane under usual Peterson conditions.[23] Another significant feature of this reaction is that it proceeds under mild and almost neutral conditions via metal-free carbanionic species and, therefore, the reaction could be applied to compounds possessing base- or acid-sensitive functionalities, such as chloro, alkoxy, alkoxycarbonyl, and cyano groups.

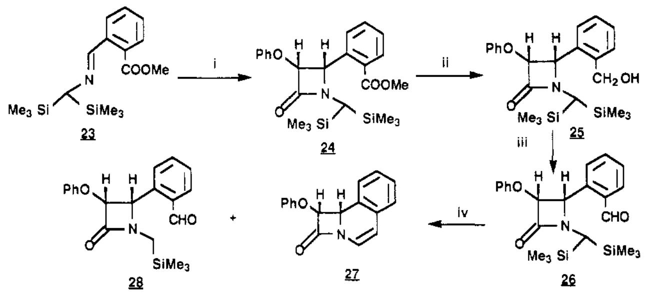
In spite of the fact that the reaction mechanism is not clear at present, it is possible to assume[7b] (Scheme II) that the reaction is initiated by fluoride ion to generate a α-silyl carbanion, which then reacts with the carbonyl compound **1** to give the corresponding β-silylethoxide. Further elimination of (trimethylsilyl)alkoxide affords the corresponding alkene with regeneration of the catalyst. Alternatively, the reaction could be also catalyzed by the in situ formed β-silylethoxide with concomitant formation of the α-silyl carbanion and subsequent propagation by the (trimethylsilyl)alkoxide generated in the reaction media. In fact, bis(trimethylsilyl)acetonitrile reacted with 4-methylbenzaldehyde in THF, under sodium methoxide catalyst, to afford the corresponding cinnamonitrile in 77% yield (Table III). Under these conditions, the major product was the cis isomer (E/Z ratio, 16/84), which contrasts with the E/Z ratio obtained when the reaction was carried out by means of TASF catalysis (E/Z ratio, 80/20, entry c in Table I). When this reaction was tested using potassium *tert*-butoxide as catalyst, the cinnamonitrile was obtained in 68% yield as a mixture of trans and cis isomers in a ratio 66/34, respectively. Similarly, reaction between bis(trimethylsilyl)(phenylsulfonyl)methane (**10**) and 4-methoxycarbonylbenzaldehyde under methoxide catalysis afforded the corresponding vinyl sulfone in 67% yield (E/Z ratio, 100/0). These results clearly support the proposed mechanism.

Finally, in connection with an approach to the synthesis of benzofused tricyclic β-lactams,[25] we have tested the

Scheme II



Scheme III[a]



[a] Reagents and conditions: (i) $PhOCH_2COCl$, NEt_3, CH_2Cl_2, room temperature, 2 h; (ii) $NaBH_4$, EtOH reflux, 1 h; (iii) NDC, pyridine, CH_2Cl_2, room temperature, 1 h; (iv) TASF, THF, room temperature, 1.5 h.

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potential of this Peterson type alkenation in intramolecular cyclizations. For this purpose, the β-lactam **24**, prepared by reaction between phenoxyacetyl chloride and the imine **23** under standard conditions,[26] was subjected to reduction with sodium borohydride in refluxing ethanol[27] to give the β-lactam **25** in 50% isolated yield together with the monodesilylated product of **25** in 7% yield (Scheme III). After separation by column chromatography, the hydroxy compound **25** was efficiently oxidized[28] to the aldehyde **26** in 88% yield. Attempted direct reduction of the ester group in **24** into the aldehyde **26** by standard procedures[29] was unfruitful. The aldehyde **26** thus prepared was then subjected to TASF-induced desilylative cyclization, giving as the main isolated product the tricyclic β-lactam **27** in 40% yield. As expected, **26**, upon treatment with lithium diisopropylamide or *n*-butyllithium in THF as solvent, did not lead to the cyclized product **27**. Alkyllithium addition to the carbonyl group and β-lactam cleavage were observed under these Peterson reaction conditions. Particularly noteworthy is that the presently described synthesis constitutes a tactically and conceptually new approach for the construction of a tricyclic system in β-lactam chemistry which could be readily extended to the synthesis of bicyclic β-lactams, like carbapenems.[30]

From the results reported here, it is clear that this new version of the Peterson reaction[31] could be applied to a wide variety of inter and intramolecular processes, which may be readily extended to other synthetic applications.

Experimental Section

Melting points were determined on Mettler FPGI instrument and are uncorrected. Proton nuclear magnetic resonance spectra and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer. All chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane. Infrared (IR) spectra were recorded on a Shimadzu IR-435 spectrometer. Mass spectra were obtained using a Hewlett-Packard 5930 A spectrometer operated at 70 eV. Microanalytical data were obtained in these laboratories. Commercially available compounds were used in this work without further purification or were prepared by literature procedures. Trimethylchlorosilane was distilled over magnesium. Hexane was dried and purified by distillation. Tetrahydrofuran was distilled over sodium and benzophenone (indicator). Methylene chloride was shaken with concentrated sulfuric acid, dried over potassium carbonate, and distilled.

General Procedure for Alkene Formation. Aldehydes or ketones (3mmol) and compounds **5–13** (3.5mmol) were mixed at 0–5 °C in 5 mL of anhydrous tetrahydrofuran or methylene chloride, containing molecular sieves (4A), and a catalytic amount of TASF (10% equiv) was added. Instantaneously, a dark color developed with slight exothermicity, and the reaction mixture was allowed to stand at room temperature. After being stirred at the same temperature for 1–2 h, the reaction mixture was quenched with trimethylchlorosilane (0.5 mL) and diluted with methylene chloride. The mixture was washed with 0.1 N HCl and then with water. The organic layer was separated and dried. Evaporation of the solvent under reduced pressure gave the corresponding alkene, which was purified by crystallization or Kugelrhör distillation.

Unless otherwise stated, results in Tables I and II were obtained by similar reaction and workup procedures.

Bis(trimethylsilyl)acetonitrile (7). To a stirred hexane solution of 1.6 M *n*-butillithium (66 mL, 105.6 mmol) in anhydrous tetrahydrofuran (70 mL) was added (trimethylsilyl)acetonitrile (7.0 mL, 50 mmol) dropwise at −78 °C. After the mixture was stirred for 30 min, trimethylchlorosilane (13 mL, 100 mmol) was added, and the sirring was continued for 10 min at −78 °C and then at room temperature for at least 30 min. The reaction mixture was poured into NH_4Cl (150 mL, saturated solution), vigorously stirred for 5 min, and then diluited with water (300 mL). The organic layer was separated and dried ($MgSO_4$). Evaporation of the solvents gave bis(trimethylsilyl)acetonitrile (**7**). Yield: 8.0 g (86%). Bp: 102–103 °C (16 Torr) [lit.[24] bp 92 °C (12 Torr)]. ^{1}H NMR ($CDCl_3$) δ ppm: 1.08 (s, 1 H, CH), 0.15 (s, 18 H, $SiMe_3$).

(*E*)-Cinnamonitrile. A solution of benzaldehyde (0.21 g, 2 mmol) and bis(trimethylsilyl)acetonitrile (0.46 g, 25 mmol) in anhydrous methylene chloride (10 mL containing molecular sieves (4A) was cooled at −100 °C (liquid N_2/methanol bath). Then, TASF (50 mg, cat.) was added, and the mixture was stirred at this temperature for 30 min, after which it was suddenly warmed at 40 °C (water bath) and quenched with trimethylchlorosilane (0.5 mL). Workup as above afforded a crude which consists in (*E*)-cinnamonitrile (95%) [^{1}H NMR: δ 5.71 ppm (d, J = 15 Hz, $=$CHCN)] and (*Z*)-cinnamonitrile (5%) [^{1}H NMR: δ 5.22 ppm (d, J = 12 Hz, $=$CHCN)]. After Kügelrohr distillation, (*E*)-cinnamonitrile was obtained. Yield: 0.23 g (90%). Bp: 120–123 °C (20 Torr) [lit.[32] bp 115 °C (12 Torr)].

Vinylsilanes 20. General Procedure. A mixture of carbonyl compound (3 mmol) and tris(trimethylsilyl)methane (**13**) (3.5 mmol) were mixed in 5 mL of anhydrous tetrahydrofuran containing molecular sieves (4A), and the mixture was heated at reflux. Then, a catalytic amount of TASF (10% equiv) was added. After being stirred under reflux for 1–2 h, the reaction mixture was cooled and diluted with methylene chloride. The mixture was washed with 0.1 N HCl and then with water. The organic layer was separated and dried. Evaporation of the solvent under reduced pressure gave the corresponding vinylsilane, which was purified by Kügelrohr distillation.

4-Methyl-*N*-(4′-methoxyphenyl)-3-phenoxy-4-[2′-(phenylthio)vinyl]azetidin-2-one (18l). The general procedure was followed starting from *cis*-4-formyl-4-methyl-*N*-(4′-methoxyphenyl)-3-phenoxyazetidin-2-one (0.31 g, 1.0 mmol) and **9** (0.40 g, 1.5 mmol). After workup and flash chromatography (silica gel; eluant: hexane/CH_2Cl_2, 3/1) an equimolar mixture of (*E*)- and (*Z*)-vinyl sulfides **18l** was obtained. Yield: 0.24 g (58%) (syrup). ^{1}H NMR (δ ppm, $CDCl_3$) [*E* isomer]: 6.9–7.5 (m, 14 H, arom), 6.497 (d, J = 15.3 Hz, CH), 5.79 (d, J = 15.3 Hz, CH-S), 5.05 (s, 1 H, CH), 3.80 (s, 3 H, MeO), 1.85 (s, 3 H, Me). [*Z* isomer]: 6.9–7.5 (m, 14 H, arom), 6.53 (d, J = 10.8 Hz, CH), 5.69 (d, J = 10.8 Hz, CH-S), 5.06 (s, 1 H, CH), 3.79 (s, 3 H, MeO), 1.99 (s, 3 H, Me). MS (m/z) = 418 (M^+).

Preparation of *cis*-3-Phenoxy-4-[2-(methoxycarbonyl)phenyl]-1-[bis(trimethylsilyl)methyl]azetidin-2-one (24). To a cooled (0–5 °C) solution of the imine **23** (10 mmol) and triethylamine (2.52 mL, 18 mmol) in methylene chloride (15 mL) was added a solution of phenoxyacetyl chloride (2.07 mL, 15 mmol) in methylene chloride (5 mL). The resulting mixture was stirred at room temperature for 2 h. Then, the reaction mixture was washed with water (2 × 20 mL) and 0.1 N HCl (2 × 20 mL). The organic layer was separated and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave a residue, which was crystallized from ethanol. Yield: 3.65 g (80%). Mp: 118–120 °C (from ethanol). IR (KBr) ν 1750 (C=O), 1714 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.81–7.93 (m, 9 H, arom), 6.02 (d, 1 H, J = 4.8 Hz, NC*H*Ar), 5.45 (d, 1 H, J = 4.8 Hz, PhOC*H*), 3.86 (s, 3 H, OCH_3), 2.23 (s, 1 H, NC*H*$SiMe_3$), 0.28 (s, 9 H, $SiCH_3$), 0.14 (s, 9 H, $SiCH_3$). Anal. Calcd for $C_{24}H_{33}O_4NSi_2$: C, 63.24; H, 7.31; N, 3.07. Found: C, 63.76; H, 7.44; N; 3.13.

Preparation of 4-[2-(Hydroxymethyl)phenyl]-3-phenoxy-1-[bis(trimethylsilyl)methyl]azetidin-2-one (25). To a suspension of the β-lactam **24** (4.56 g, 10 mmol) in ethanol (50 mL)

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was added $NaBH_4$ (1.90 g, 50 mmol), and the resulting mixture was refluxed for 1 h. Then the reaction mixture was poured into 0.1 N HCl (150 mL) and extracted with methylene chloride (2 × 75 mL). The organic layer was washed with $NaHCO_3$ (50 mL, saturated solution) and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave a syrup which was purified by a column chromatography (silica gel, 70–230 mesh, CH_2Cl_2/hexane, 1:2, and then 1:1 as eluant) to give first the title compound **25**. Yield: 2.14 g (50%). Mp: 112–114 °C (CCl_4/hexane). IR (KBr) ν 3376 (OH), 1726 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ (ppm): 6.76–7.59 (m, 9 H, arom), 5.46 (d, 1 H, J = 4.8 Hz, PhOC*H*), 5.36 (d, 1 H, J = 4.8 Hz, NC*H*Ar), 4.70 (dd, 1 H, J = 12.6 Hz, J' = 7.2 Hz, CH_2OH), 4.61 (dd, 1 H, J = 12.6 Hz, J' = 4.8 Hz, CH_2OH), 2.21 (s, 1 H, $CHSiMe_3$), 1.43 (dd, 1 H, J = 4.8 Hz, J' = 7.2 Hz, O*H*), 0.26 (s, 9 H, $SiCH_3$), 0.16 (s, 9 H, $SiCH_3$). Anal. Calcd for $C_{23}H_{33}O_3NSi_2$: C, 64.58; H, 7.79; N, 3.27. Found: C, 64.87; H, 7.83; N, 3.30, and then 0.25 g (7%) of monodesilylated derivative of **25**. ^1H NMR ($CDCl_3$) δ (ppm): 6.71–7.41 (m, 9 H, arom), 5.46 (d, 1 H, J = 4.8 Hz, PhOC*H*), 5.28 (d, 1 H, J = 4.8 Hz, NC*H*Ar), 4.57 (s, 2 H, CH_2OH), 2.95 (d, 1 H, J = 15.3 Hz, NCH_2SiMe_3), 2.40 (d, 1 H, J = 15.3 Hz, NCH_2SiMe_3), 2.25 (s, 1 H, OH), 0.11 (s, 9 H, $SiCH_3$).

Preparation of 4-(2′-Formylphenyl)-3-phenoxy-1-[bis(trimethylsilyl)methyl]azetidin-2-one (26). This compound was prepared using 3-carboxypyridinium dichromate/pyridine system following our procedure.[28] Yield: 1.12 g (88%). Mp: 126–128 °C (MeCN/H_2O). IR (KBr) ν 1754 (C=O), 1688 cm^{-1} (CHO). ^1H NMR ($CDCl_3$) δ (ppm): 9.99 (s, 1 H, CHO), 6.69–7.72 (m, 9 H, arom), 6.19 (d, 1 H, J = 4.8 Hz, NC*H*Ar), 5.45 (d, 1 H, J = 4.8 Hz, PhOC*H*), 2.15 (s, 1 H, $CHSiMe_3$), 0.29 (s, 9 H, $SiCH_3$), 0.15 (s, 9 H, $SiCH_3$). Anal. Calcd for $C_{23}H_{31}O_3NSi_2$: C, 64.88; H, 7.35; N, 3.29. Found: C, 64.50; H, 7.28; N, 3.43.

Preparation of Benzocarbacephem 27. To a stirred solution of the aldehyde **26** (1.06 g, 2.5 mmol) in anhydrous tetrahydrofuran (13 mL) containing molecular sieves (1 g, 4A) was added, under nitrogen, tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF, 10 % mol). Immediately, a dark coloration appeared with slight exothermicity. After 90 min of stirring at room temperature, trimethylchlorosilane (0.33 mL, 2.6 mmol) was added and, after workup, the reaction crude was chromatographied (silica gel; eluant: CH_2Cl_2/hexane, 1/3), affording **27** [Yield: 0.26 g (40%) (syrup). ^1H NMR (δ ppm, $CDCl_3$): 7.02–7.35 (m, 9 H, arom), 6.64 (d, 1 H, J = 7.2 Hz, ArC*H*=), 6.16 (d, 1 H, J = 7.2 Hz, NC*H*=), 5.91 (d, 1 H, J = 4.2 Hz, NC*H*Ar), 5.14 (d, 1 H, J = 4.2 Hz, PhOC*H*). MS (m/z) = 353 (M^+)] and **28** [Yield: 0.04 g (5%). ^1H NMR (δ ppm, $CDCl_3$): 9.96 (s, 1 H, CHO), 6.71–8.00 (m, 9 H, arom), 6.08 (d, 1 H, J = 4.8 Hz, NCHAr), 5.58 (d, 1 H, J = 4.8 Hz, PhOCH), 3.09 (d, 1 H, J = 15.3 Hz, NCH_2SiMe_3), 2.45 (d, 1 H, J = 15.3 Hz, NCH_2SiMe_3), 0.12 (s, 9 H, $SiMe_3$)].

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Electrochemical Coupling of Activated Olefins and Alkyl Dihalides: Formation of Cyclic Compounds

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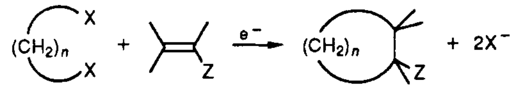
The electrochemical coupling of dimethyl maleate, methyl cinnamate, 4-phenyl-3-buten-2-one, or methyl acrylate with dibromomethane, 1,3-dibromopropane, 1,4-dibromobutane, or other substituted alkyl dihalides gave satisfactory yields of cyclic products. The reactions were performed in an undivided cell fitted with a sacrificial aluminum anode, in *N*-methylpyrrolidone (NMP), at constant current, and at room temperature. The role of the anodically generated metallic ions in this cyclocondensation has been evidenced.

Cyclic and polycyclic compounds have great importance in synthetic chemistry, and new methods are constantly sought out with the aim of obtaining more simple and more efficient routes to cycle formation. Whereas ring closure of α–ω difunctional compounds is a straightforward method, more challenging is ring forming through bimolecular coupling, especially for cyclopentanation. Some efficient electrochemical intramolecular ring-forming reactions have already been described.[1] We thought in the wake of recent progress associated with the use of consumable anodes[2] that electroreductive organic chemistry could also offer a useful approach to bimolecular cyclocondensation. We describe here the synthesis of three-, five-, and six-membered alicyclic products by electroreductive coupling of electron-deficient olefins and alkyl dihalides (eq 1).



(1)

X = Br, Cl; n = 1–4; Z = electron-withdrawing group

Results

Results of the coupling reaction of various olefins and alkyl dihalides are given in Table I. Two typical experimental conditions were adopted according to the relative reduction potential of both the olefin and the opposed dihalide.[3] Thus, for the reaction involving dimethyl maleate and 1,3-dibromopropane, as an example of readily reduced olefin as compared to the dihalide, 2 equiv of 1,3-dibromopropane for 1 equiv of dimethyl maleate was mixed, in the range 0.3–0.8 M olefin, in *N*-methyl-

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