1460, 1253, 1205, 1167, 1015, 782 cm^{-1}; NMR 3.73 (s, 3 H), 6.43 (br, s, 1 H), 6.75 (m, 2 H), 6.90 (m, 2 H); ^{13}C NMR 185.7 (s), 165.5 (s), 141.8 (d), 133.5 (d), 133.1 (d), 131.9 (d), 116.9 (d), 55.5 (q). This workup was necessary to remove the iron.

4b: 45% yield; UV (MeOH) 245, 253, 290, 307 nm (sh); IR 3400, 2900, 1680 (w), 1630, 1540 (br), 1200, 1160 cm^{-1}; NMR 2.15 (s, 3 H), 3.70 (s, 3 H), 6.35 (m, 1 H), 6.65 (m, 2 H), 6.80 (m, 1 H); MS, m/z 150 (M^+), 122, 121.

4c:[4] 48% yield; UV (MeOH) 238 (br), 281, 288, 305 (sh) nm; IR 3450, 2950, 1700 (w), 1660, 1590, 1540, 1210 cm^{-1}; NMR 2.25 (s, 3 H), 3.75 (s, 3 H), 6.30–7.00 (m, 4 H); MS, m/z 150 (M^+), 122, 121.

Registry No. **1a**, 18406-12-7; **1b**, 88841-50-3; **1c**, 88841-49-0; **2a**, 88780-25-0; **2b**, 88780-26-1; **2c**, 88780-27-2; **3a**, 88780-28-3; **3b**, 88780-29-4; **3c**, 88780-30-7; **4a**, 54445-60-2; **4b**, 88780-31-8; **4c**, 88780-32-9; **5**, 66967-07-5; **6**, 88780-33-0; **7**, 88780-34-1; **8**, 88780-35-2; **9**, 88780-36-3.

Solid–Liquid Phase-Transfer Catalysis Reactions without Solvent; Very Mild Conditions for β-Eliminations

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We have recently shown that alkylations of acetate[1,2a] and indole anions[1,2b] can be run without solvent in the presence of catalytic amounts of quaternary tetraalkylammonium salts (solid–liquid PTC conditions). These reaction conditions present many advantages: no need for organic solvent, low temperatures, and short reaction times as well as very easy workup.

We describe here the extension of this method to base-induced β-eliminations. Secondary halide dehydrohalogenations are well-known either in solution[3] or under classical PTC conditions.[4] 2-Bromooctane behavior was studied as a typical weak halide which exhibits the possibility of competitive Saytzeff vs. Hofmann orientations.

Experimental Section

All reagents were purchased and used without further purification. 2-Bromooctane (1.93 g, 10 mmol) is added to 25 mmol of base finely ground in a blender and 2 % mol (relative to the base) of tetraalkylammonium salt. After being vigorously stirred for 10 min with a mechanical stirrer, the mixtures are allowed to sit for the indicated periods at the appropriate temperature (see tables). Organic products were removed by a simple filtration on Florisil (on which ammonium salts remain adsorbed) after addition of 50 mL of diethyl ether. They were identified by comparison with authentic samples and analyzed by GPC (internal standard): (OV 1 column) 25 m, 0.1–0.15 μm, carrier N_2, p = 0.5 kg, 40 °C, t_R 1-octene 4.2 min, t_R *trans*-2-octene 4.6 min, *cis*-2-octene 4.8 min, t_R nonane (standard) 8.6 min; (SE 30 column) 1 m, 15% Chromosorb WAW 020–025, carrier N_2, p = 1.2 kg, 80 °C, t_R nonane (standard) 1.1 min, t_R 2-bromooctane 3.7 min.

Table I. Influence of the Type of Ammonium Salt in the Reaction of 2-Bromooctane and *t*-BuOK under PTC Conditions[a]

	starting material, %	octenes, %
	68	25
NBu_4I	69	31
NBu_4Br	53	40
NBu_4Cl	66	28
NBu_4HSO_4	80	17
$C_6H_5CH_2NEt_3Br$	87	13
$C_{16}H_{33}NMe_3Br$	54	40
Aliquat 336	4	92

[a] Reaction conditions: 2% ammonium salt, 2.5 equiv/mol of *t*-BuOK for 2 h at room temperature.

Results

The influence of the nature of the tetraalkylammonium salts is examined for the 2-bromooctane reaction with *t*-BuOK (2 h at room temperature) (Table I). Aliquat 336 (essentially $Oct_3MeN^+Cl^-$)[5] appears to be the most efficient reagent: quasi-quantitative β-elimination is observed.

The orientation of the reaction (Table II) is only slightly affected by the nature of ammonium salts (1-octene/2-octenes > 80:20), whereas Aliquat 336 is 66:34.

On the other hand, the orientation is strongly dependent on the nature of the base: the 1-octene/2-octenes ratios increase according to $tBuO^- > HO^- > EtO^- \gtrsim MeO^-$ (Table III).

Discussion

t-BuOK-induced reactions are quantitative in 20 h at room temperature in the absence of any tetraalkylammonium salts. They can be catalyzed by 2% Aliquat (reaction completion within 2 h). The 1-octene/2-octene ratios remain constant independent of reaction times and temperatures, implying that there is no further olefin equilibration under these conditions.

With the other bases, no reaction takes place for 20 h at room temperature unless Aliquat 336 is added; yields are thus >92%. As previously proposed for acetate alkylation,[1,2a] we are certainly dealing with solid–liquid PTC reactions without solvent: the reactive basic species are the loose $RO^-//N^+R_4$ ion pairs, the organic phase being constituted by 2-bromooctane and octenes. The cation

$$RO^-, M^+ + R_4N^+, X^- \rightleftarrows RO^-//^+NR_4 \text{ (soluble in 2-bromooctane or 1-octene + 2-octenes)}$$

effect (MeOK more efficient than MeONa) is consistent with such an explanation: in connection with a lower lattice energy in the K salt,[6] the equilibrium must be more shifted to the ammonium pairs.

Hofmann vs. Saytzeff Orientation. The 1-octene/2-octene ratios are markedly dependent on the nature of the base. These results are compared (Table IV) to the results obtained in solvents with 2-bromohexane.

Regioselectivites of elimination at room temperature in our conditions (no added solvent) are very close to those obtained when the reactions are performed at reflux in

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Table II. Product Distribution in the Reaction of 2-Bromooctane with *t*-BuOK under PTC Conditions[a]

	starting material, %	olefins, %	1-octene, %	2-octenes, % trans	2-octenes, % cis
	6	94	83	8	9
NBu_4Br[b]		95	72	19	9
$C_6H_5CH_2NEt_3Br$[b]	2	93	80	10	10
$C_{16}H_{33}NMe_3Br$[b]	3	93	82	9	9
Aliquat 336		98	66	25	9

[a] Reaction conditions: 2% ammonium salt, 2.5 equiv/mol of *t*-BuOK for 20 h at room temperature. [b] Same results in 5 h at 85 °C.

Table III. Influence of the Base in the Reaction of 2-Bromooctane with B^-M^+ under PTC Conditions[a]

B^-M^+	catalyst (2%)	time, h	starting material, %	1-olefins, %	1-octene, %	2-octene, % trans	2-octene, % cis
HOK		20	96	4			
	NBu_4Br	20	95	5			
	Aliquat	2	63	35	42	48	10
	Aliquat	20		93	42	46	12
t-BuOK		20	6	94	83	8	9
	Aliquat	2	4	92	65	26	9
MeOK		20	100				
	Aliquat	2	47	49	33	55	12
	Aliquat[b]	20		95	33	54	13
MeONa		20	100				
	Aliquat	2	72	25	34	55	11
	Aliquat	20	2	92	34	54	12
EtONa		20	100				
	Aliquat	2	53	43	36	52	12
	Aliquat	20		92	34	54	12

[a] Reaction conditions: 2.5 equiv/mol of B^-M^+ at room temperature. [b] A same result is obtained in the same conditions from MeOK preformed in situ by reacting MeOH and KOH.

Table IV. Comparison of Our Results with Those Obtained in Solution[7-10]

	PTC conditions without solvent: catalyst	yield, %	1-alkene:2-alkenes	solutions: solvent	yield, %	1-alkene:2-alkenes
t-BuOK		94	83:17	*t*-BuOH, 100 °C[7]	94	80:20
	Aliquat	98	66:34	C_6H_6, 130 °C[9]		80:20
				Me_2SO, 50 °C[10]	72	47:53
MeONa	Aliquat	92	34:66	MeOH, 100 °C[7]	75	28:72
EtONa	Aliquat	92	34:66	EtOH, 80 °C[8]	80	25:75

Table V. Other Recent Methods for Dehydrohalogenation of 2-Bromooctane

basic reactants	time, h	temp, °C	yield, %
KF + phosphonium salts[11]	76	120	64
KF + crown ether (C_6H_6)[12]	($t_{1/2}$ = 240 h)	90	68
polymer supported F^-[13] (pentane)	30	36	73
t-BuOK + crown ether[14] (petroleum ether)	3	60	76
NaOH + NBu_4Br (H_2O-C_6H_6)[15]	48	80	86
KOH/crown ether (C_6H_6)[16]	18	80	80
KOH + PEG 600 (C_6H_6)[16,17]	2	80	82
KOH + PEG 600 + crown ether (C_6H_6)[16]	2	80	100

alcoholic media. Thus, with *t*-BuOK, whereas the results are very similar in our conditions to those obtained in *t*-BuOH solution,[7] the results are very different in Me_2SO[10] or when classical PTC is used.[11-17]

The observed regioselectivites can be interpreted in terms of steric effects as when the reaction is run in solution: the smaller the basic species, the easier the formation of 2-octenes due to attack at the most hindered site. In such a way, the effect of Aliquat on the orientation can be considered by the intervention of a loose ion pair $t\text{-BuO}^-//N^+R_4$, of smaller size than the higher aggregates $(t\text{-BuO}^-K^+)_n$.[3a]

Comparison with Other Methods. In addition to classical experiments performed in solvents, alternative methods for β-eliminations (solid–liquid PTC or triphase catalysis) have been proposed recently. When applied to

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the case of 2-bromooctane, representative results are indicated in Table V.

The procedures we describe here are milder, more efficient, less expensive and more convenient (smaller reaction times, lower temperatures, easier workup) than those published previously. The stereo- and regioselectivities obtained are very close to those observed with alkoxide in alcohol at reflux.

These results contitute a new illustration of the potential in organic synthesis of reactions performed under solid–liquid PTC conditions in the absence of solvent.

Registry No. 2-Bromooctane, 557-35-7.

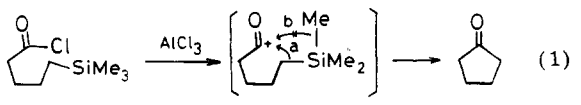
Communications

A Cyclopentanone Annulation via Intramolecular Acylation of Alkylsilanes

Summary: A facile construction of cyclopentanones is achieved via a ring closure of 5-(trimethylsilyl)alkanoyl chlorides under the influence of $AlCl_3$.

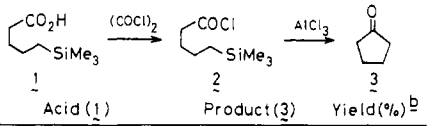
Sir: Cyclopentanones are widely found in naturally occurring products, and exploration of new procedures for construction of such frameworks from readily available acyclic precursors is still required in natural product synthesis. Among the many approaches, a ring closure by the combination of the acyl cation and the alkyl anion equivalent would be one of the most straightforward methodologies (Scheme I).

To effect this transformation, the alkyl anion equivalent depicted in Scheme I should be compatible with the nucleophilic carbonyl functionality in the same molecule. For such purposes, silicon-substituted alkyl groups seem to be employed as the incipient anion because the carbon–silicon bond is weakly polarized to fulfill the above requirement. Although the utility of unsaturated organosilicon compounds such as alkenyl-, allyl-, and arylsilanes has been amply demonstrated,[1] synthetic reactions dealing with simple alkyl-silicon bonds have not been elucidated up to now.[2] Since alkylsilanes are considerably stable under various circumstances, their reactions are alluded to require drastic conditions. Selective transfer of an alkyl group from an alkyltrimethylsilane is also quite problematic. However, we disclose here that Lewis acid mediated intramolecular acylation of alkylsilanes[3,4] works quite well for the preparation of a variety of cyclopentanones. The reaction proceeds via a selective fission of an appropriate carbon–silicon bond to yield the corresponding cyclopentanone (eq 1).

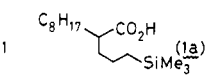
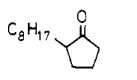
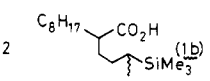
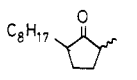
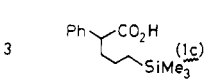
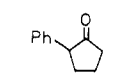
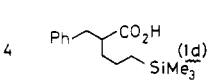
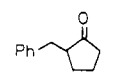
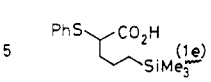
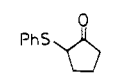
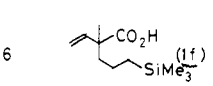
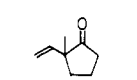
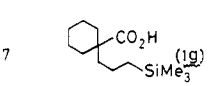
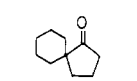


(1)

Table I. Cyclopentanone Synthesis by Intramolecular Acylation of 5-(Trimethylsilyl)alkanoyl Chlorides[a]



1 2 3

Run	Acid (1)	Product (3)	Yield (%)[b]
1			87 (92)[c]
2			83
3			84
4			85
5			60[d]
6			67[e]
7			70

[a] Reactions are carried out in 0.2–0.3-mmol scale with the reactant ratio $1/(COCl)_2/AlCl_3 = 1:2:1$. [b] Overall yield from 1. Products are isolated by chromatography. [c] Reaction in 3.5-mmol scale and the product was isolated by Kugelrohr distillation. [d] Reactant ratio: $1/(COCl)_2/AlCl_3 = 1:1.5:0.75$. [e] Relatively low yield may reflect the volatility of the product.

The starting materials are readily obtained by standard methods (Scheme II). Alkylation of the dianion of carboxylic acid[5] with 3-(trimethylsilyl)alkyl bromide or iodide is a most convenient method to prepare 5-(trimethylsilyl)alkanoic acids. In others case where carboxylic acids cannot be employed (e.g., run 6), alkylation of an ester with the halide followed by hydrolysis is an alternative way.

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