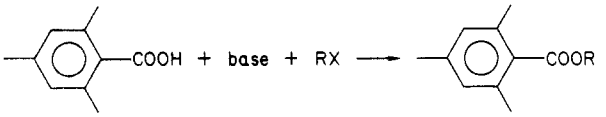
Table IV. Some Recent Preparations of Mesitoic Esters



system base–solvent	RX	time, h	temp, °C	yield,[a] %	ref
	Compound **1a**				
KOH–Aliquat 2%	CH_3I	1	20	(98)	this work
KOH–HMPA/EtOH (1:1)	CH_3I	0.5	25	96	15
NaOH–HMPA	CH_3I (4 equiv)	0.2	25	99	16
DBU[b]–CH_3CN	CH_3I	1	25	(96)	17
K_2CO_3–acetone	$(CH_3)_2SO_4$	1	56	95	18
CH_2Cl_2	Me_3O^+, BF_4^-	24	25	(90)	19
	Compound **1b**				
KOH–Aliquat 2%	C_2H_5Br	1	60	(98)	this work
NaOH–HMPA	C_2H_5I (4 equiv)	0.2		96	20
K_2CO_3–acetone	C_2H_5I	16	56	100	21
Resin AG1-8X–CH_3OH	C_2H_5I	20	65	(94)	21
K_2CO_3–silica gel $Bu_4P^+Br^-$ (gas–liquid PTC)	C_2H_5Br	2 (20 torr)	170	(73)	22
CH_2Cl_2	Et_3O^+,BF_4^-	24	25	(90)	19
DBU[b]–benzene	C_2H_5I	2	25	80	23
	Compound **1c**				
KOH–Aliquat 2%	C_4H_9Br	2	85	(88)	this work
Resin AG1-8X–CH_3OH	C_4H_9Br	25	65	8	21
Resin AG1-8X (Na salt)–toluene/water	C_4H_9Br	24	75	53	21
grafted resin on polystyrene–toluene/water	C_4H_9Br	92	75	93	21

[a] Isolated yields are in parentheses. [b] DBu = 1,5 diazabicyclo[5.4.0]undec-5-ene.

presence during alkylation by ethyl bromide: this fact is confirmation for a solid–liquid PTC process.

With regard to the choice of the base, the use of KOH leads to satisfactory results. However, with rather poor electrophilic reagents (e.g., n-$C_{16}H_{33}Br$), the utilization of powdered K_2CO_3 seems to give better results. Quantitative yields are thus obtained (cf. runs 17 and 18). This observation is certainly due to a partial saponification of the product esters **1d** and **1e** by KOH–Aliquat at 85 °C (compare runs 13 and 14).

The results constitute a new illustration in organic synthesis of the potential of reactions performed under solid–liquid PTC conditions in the absence of solvent. They emphasize the exceptional basicity and nucleophilicity toward carbonyl esters group of the [solid KOH + 2% Aliquat 336] system.

Experimental Section

Since the reactions performed were all similar in many respects, only typical reactions are described as specific examples.

Preparation of *n*-Octyl Mesitoate. To a mixture of 0.5 mmol of Aliquat 336 (240 mg) and 25 mmol of finely ground KOH, which contained 15% w/w water (1.61 g) was added 11 mmol of mesitoic acid (1.804 g) in a Pyrex flask. After shaking 5 min, 10 mmol of *n*-octyl bromide (1.93 g) was added, and the mixture was shaken for 5 min at room temperature. The reaction mixture was left, without any shaking or stirring, in an oil bath at 85 °C for 2 h. The organic products were removed with 50 mL of diethyl ether and the mixture was filtered through 5 g of Florisil (to retain mineral salt and Aliquat 336). The esters were analyzed by GLC with an internal standard (butyl phthalate in this case). The product was isolated after solvent evaporation and, eventually, subjected to Florisil (or silica gel) column chromatography with pentane as an eluant to give *n*-octyl mesitoate (2.416 g, 88%). The purity of the ester was checked by GLC, IR, NMR, and analysis.

Saponification of Methyl Mesitoate. Methyl mesitoate (1.78 g, 10 mmol) was added to a Pyrex flask containing a mixture of 1 mmol of Aliquat 336 (480 mg) and 50 mmol of finely ground KOH (3.22 g), which contained 15% w/w water. After 5 min of agitation at room temperature, the flask was left, in an oil bath at 85 °C for 5 h, without any shaking or stirring. Starting ester and Aliquat were extracted into 50 mL of diethyl ether. The product mesitoic acid was obtained after addition of 50 mL of water and acidification with diluted HCl. The precipitate was then removed and dried (1.525 g, 93%). It was characterized by its melting point (153–154 °C)[11] and IR and ^1H NMR spectra.

Spectral Data of Esters. ^1H NMR spectra were recorded with a Perkin-Elmer R 32 spectrometer and chemical shifts are expressed as δ relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 1310.

Methyl mesitoate (1a):[19] NMR ($CDCl_3$) 2.30 (s, 9 H), 3.90 (s, 3 H), 6.90 (s, 2 H); IR (film) 1725 cm^{-1}.

Ethyl mesitoate (1b):[19,23] NMR ($CDCl_3$) 1.35 (t, 3 H), 2.30 (s, 9 H), 4.35 (9, 2 H), 6.90 (s, 2 H); IR (film) 1725 cm^{-1}.

***n*-Butyl mesitoate (1c):**[21] NMR ($CDCl_3$) 0.8–1.9 (m, 7 H), 2.30 (s, 9 H), 4.35 (t, 2 H), 6.90 (s, 2 H); IR (film) 1725 cm^{-1}.

***n*-Octyl mesitoate (1d):** NMR ($CDCl_3$) 0.8–1.9 (m, 15 H), 2.30 (s, 9 H), 4.35 (t, 2 H), 6.90 (s, 2 H); IR (film) 1725 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.26; H, 10.14. Found: C, 77.90; H, 10.19.

***n*-Cetyl mesitoate (1e):** mp 37–38 °C; NMR ($CDCl_3$) 1.0–1.4 (m, 31 H), 2.30 (s, 9 H), 4.35 (t, 2 H), 6.90 (s, 2 H); IR (film) 1725 cm^{-1}. Anal. Calcd for $C_{26}H_{44}O_2$: C, 80.41; H, 11.34. Found: C, 80.54; H, 11.30.

GLC of Esters. Products were analyzed with an internal standard on a 15% SE30 column, length = 1 m, carrier gas N_2, p = 1.2 kg (oven temperature, t): **1a**, 120 °C, 2.82 min; **1b**, 120 °C, 4.12 min; **1c**, 140 °C, 5.52 min; **1d**, 200 °C, 3.46 min; **1e**, 270 °C, 4.81 min.

Registry No. a, 2282-84-0; b, 1754-55-8; c, 70116-77-7; d, 99921-94-5; e, 99921-95-6; MeI, 74-88-4; EtBr, 74-96-4; Et_2SO_4, 64-67-5; BuBr, 109-65-9; n-$C_8H_{17}Br$, 111-83-1; n-$C_{16}H_{33}Br$, 112-82-3; $(C_8H_{17})_3NMe^+Cl^-$, 5137-55-3; mesitoic acid, 480-63-7.

Calixarenes. 18. Synthesis Procedures for *p*-*tert*-Butylcalix[4]arene

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Calixarenes, which are stoma-containing macrocyclic compounds with shapes ranging from baskets to wheels,[1] were first synthesized by Zinke and Ziegler[2] in 1941 by the

(1) For reviews of the calixarenes, see: Gutsche, C. D. *Acc. Chem. Res.* **1983**, *16*, 161; *Top. Curr. Chem.* **1984**, *123*, 1.

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base-induced condensation of a *p*-alkylphenol with formaldehyde. Subsequent publications by Zinke et al.[3-5] describing the reaction with a variety of phenols, including *p*-methyl-, *p-tert*-butyl, *p-tert*-amyl-, *p*-(1,1,3,3-tetramethylbutyl)-, *p*-cyclohexyl-, *p*-benzyl-, and *p*-phenylphenol, seemed to indicate that the cycle tetramer (the calix[4]arene) is the sole product in every case. An investigation some years later by Cornforth and co-workers,[6] however, showed that more than one product can be formed, and recent studies by Gutsche and co-workers[7] have demonstrated that the outcome of the reaction can be strongly influenced by the reaction conditions. The condensation of *p-tert*-butylphenol with formaldehyde has been studied in considerable detail, and it constitutes the best and most useful example of a calixarene-forming reaction. However, various workers using the procedures that we have published[7] have frequently encountered difficulties in duplicating the reported results, as have workers in our own laboratories. The purpose of the present investigation is to establish a set of procedures that we hope can be reproduced without complication for the preparation of *p-tert*-butylcalix[4]arene.

***p-tert*-Butylcalix[4]arene.** Cyclic tetramers have been obtained only from a few phenols, principally those carrying a highly branched *p*-alkyl substituent. Small groups such as methyl, larger groups such as adamantyl, and groups such as benzyl and phenyl all give rise to larger oligomers and generally much less tractible reaction mixtures. Among the phenols carrying highly branched *p*-alkyl substituents, *p-tert*-butylphenol appears to be the best for producing easily purified reaction mixtures, although the yields of its cyclic tetramer have varied from 0% to as high as 35%. The reasons for these variations seemed quite mysterious, and the present work was undertaken to try to dispel some of this mystery.

The "modified Zinke–Cornforth" procedure[7] for the preparation of *p-tert*-butylcalix[4]arene is a several-step sequence involving (a) heating a solution of *p-tert*-butylphenol, 37% formaldehyde, and aqueous NaOH for 45 h at 50–55 °C, (b) heating this same mixture at 110–120 °C for 2 h, during which time water is driven off and a yellow solid remains, (c) "neutralizing" the solid with aqueous HCl and then drying it, and (d) adding the solid to Dowtherm and heating it for 2 h at 210–220 °C. We have now shown that the first step can be omitted and that what we shall refer to as the "precursor" can be prepared simply by heating a solution of *p-tert*-butylphenol, 37% formaldehyde, and base at ca. 120 °C for 2 h. One of the main factors in the failure of different workers, or even the same worker, to obtain reproducible results in the "neutralization" procedure. The precursor is a friable solid which can be ground to a powder whose particle size depends on the manner and extent of grinding. In our original procedure, presumably similar to that used by previous workers, the "finely" ground solid was triturated with aqueous HCl. A neutron activation analysis on the "neutralized precursor", however, revealed that even after extensive trituration sodium ions are retained, almost certainly as the phenoxide. Subsequent experiments have shown that completely base-free precursor fails to form calixarene upon heating, indicating that a certain amount of base is an absolute essential to induce cyclization. Also, as shown by the experiments described below, the precise amount of base present at this stage of the process plays a crucial role in determining the nature of the product. Thus, variations in the outcome of past reactions can be attributed, at least in part, to the varying extents to which NaOH was leached from the precursor. To avoid this uncertainty the neutralization process can be carried out by dissolving the initially obtained yellow solid in chloroform, thoroughly washing the chloroform solution with aqueous HCl and then several times with water, drying the solution, and removing the solvent by evaporation to leave truly neutral precursor.

Table I. Effect of Base Concentration on the Formation of *p-tert*-Butylcalix[4]arene

NaOH, equiv	yield, %	product composition
0.00	0	starting material
0.0031	25	cyclic tetramer
0.0062	47.5	cyclic tetramer
0.012	54	cyclic tetramer
0.025	58	cyclic tetramer
0.030	58	cyclic tetramer
0.035	58	cyclic tetramer
0.037	60	cyclic tetramer
0.040	57	cyclic tetramer
0.050	50	cyclic tetramer
0.10	33	cyclic tetramer
0.15	30	cyclic tetramer (18%) cyclic hexamer (12%)
0.30	60	cyclic hexamer
0.50	67	cyclic hexamer
0.70	45	cyclic hexamer

With the use of precursor neutralized in this fashion, the effect of the amount of base on the yield and purity of the cyclization product was investigated. The results, shown in Table I, indicate that when the precursor is refluxed for 2 h in the presence of NaOH the optimum amount of base is 0.03–0.04 equiv (based on the amount of phenol used). Lower concentrations produce cyclic tetramer as the only cyclized product (but in lower yield), whereas higher concentrations give increasingly larger amounts of cyclic hexamer.

With the use of 0.037 equiv of NaOH (i.e., the optimum amount of base), a study of the effect of variation in reaction time gave the following results: 0.5 h (58% yield), 1 h (59% yield), 2 h (60% yield), 10 h (44% yield). The reaction appears to be much less sensitive to time than to the amount of base used. Also, the yield of cyclic tetramer remains essentially constant as the ratio of formaldehyde to *p-tert*-butylphenol is varied from 1:1 to 5:1. However, with the larger ratios the product acquires an off-white color, whereas under the optimum conditions the crude product is a sparkling white material.

At this point it became evident that the process might be elided even further by simply mixing the required amount of base at the very beginning of the reaction and omitting the neutralization of the precursor. This proved to be entirely feasible, and the method of choice for preparing the cyclic tetramer now consists of (a) mixing *p-tert*-butylphenol, 37% formaldehyde, and ca. 0.045 equiv of NaOH, (b) heating the mixture for 1.5–2 h at 120–125 °C in a system equipped with a water separator, (c) suspending the finely divided precursor in diphenyl ether, (d) refluxing the diphenyl ether solution for 2 h under a flow of nitrogen, (e) treating the cooled reaction mixture with ethyl acetate, and (f) isolating the product by filtration to yield a glistening white crude material that is pure enough for most purposes. By means of this procedure reactions have been run on a 300-g scale with no reduction in yield,

(2) Zinke, A.; Ziegler, E. *Ber.* **1941**, *74*, 1729.
(3) Zinke, A.; Ziegler, E. *Ber.* **1944**, *77B*, 264.
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(5) Zinke, A.; Kretz, R.; Leggewie, E.; Hössinger, K. *Monatsh. Chem.* **1952**, *83*, 1213.
(6) Cornforth, J. W.; D'Arcy Hart, P.; Nicholls, G. A.; Rees, R. J. W.; Stock, J. A. *Br. J. Pharmacol.* **1955**, *10*, 73.
(7) Gutsche, C. D.; Dhawan, B.; No, K. H.; Muthukrishnan, R. *J. Am. Chem. Soc.* **1981**, *103*, 3782.

Table II. Effect of the Cation of the Base on the Yield of *p*-*tert*-Butylcalix[4]arene

base	equiv of base	reflux time, h	yield of cyclic tetramer, %
LiOH	0.03	12	37
	0.04	8	41
	0.05	7	34
	0.10	2.5	30
	0.15	1.5	30[a]
NaOH	0.03	1.5	48
	0.035	1.5	54
	0.04	1.5	54
	0.05	1.5	54
KOH	0.02	1.5	24
	0.03	2	27
	0.04	3	33
	0.05	5	48[b]
RbOH	0.03	2	29
	0.04	2	36
	0.05	2	34
CsOH	0.03	1.5	11
	0.04	3	15
	0.05	5	22

[a] Quality of product inferior. [b] TLC indicates presence of small amount of hexamer.

and there would appear to be no limit to the scale on which the cyclic tetramer can be produced. With this procedure but in some cases extending the reflux time in diphenyl ether to the point where a TLC analysis of an aliquot showed the complete disappearance of cyclic octamer (see subsequent discussion), the effect of the cation was studied. As shown by the results in Table II, NaOH appears to be the base of choice if the cyclic tetramer is the desired product. Attempts to further streamline the process by using the "Petrolite procedure", which is so useful for the preparation of the cyclic octamer, were unsuccessful. Litte or no cyclic product is obtained when *p*-*tert*-butylphenol, paraformaldehyde, and the required amount of base are refluxed in diphenyl ether for several hours.

During the study of cyclic tetrameter formation we noticed that when the precursor is heated in diphenyl ether a precipitate forms shortly after heating is commenced and long before the reflux temperature is reached. Then, as the temperature climbs, the precipitate goes back into solution. The reaction mixture remains clear at the reflux temperature, and only upon cooling does precipitate once again appear. Removal of the initial precipitate by filtration reveals it to be pure cyclic octamer containing no trace of cyclic tetramer, and we surmise from this observation that the cyclic octamer may be an obligatory precursor to cyclic tetramer. To gain further insight into this possibility a series of experiments was undertaken involving the synthesis of the cyclic octamer by the "precursor isolation method".

***p*-*tert*-Butylcalix[8]arene.** The Petrolite procedure[8] consists of refluxing a mixture of *p*-alkylphenol, paraformaldehyde, and a trace of base in xylene for several hours, cooling the mixture, and removing the product of cyclization by filtration. Under optimum conditions the product is mainly the cyclic octamer, although it is always contaminated with at least small amounts of cyclic hexamer and sometimes with cyclic tetramer as well. This fact was not made clear in our earlier description of this synthesis,[7] and the yields that we reported at that time perhaps are misleading. To explore the influence of reaction conditions on the formation of cyclic octamer, particularly in the light of the possible presence of the cyclic octamer on the pathway to the cyclic tetramer, we have used both the Petrolite procedure as well as the precursor isolation method that is described above. In the latter, the isolated precursor was added, without neutralization, to xylene, and the mixture was refluxed for 4 h. The results, as shown in Table III disclose that the crude product is always is accompanied by certain amounts of other oligomers, especially the cyclic hexamer. This necessitates several recrystallization to obtain completely pure material, and the varying melting points that have been recorded for this oligomer probably reflect varying product purities.

We have used the Petrolite procedure to make a detailed comparison of NaOH and KOH as the basic catalyst. The results indicate that over the concentration range of 0.02–0.05 equiv of base there is little difference between NaOH and KOH with respect to the yield of recrystallized product (42–49%), but it is interesting to note that the highest crude yield (75% with 0.05 equiv of KOH) gives the lowest recrystallized yield. This is attributed to the greater amount of cyclic hexamer that is formed in this instance. Since the Petrolite procedure and the precursor isolation method give very similar results and since the former is the easier procedure to carry out in the laboratory, it remains the one of choice for the synthesis of *p*-*tert*-butylcalix[8]arene.[7]

A comparison of the results shown in Tables II and III shows that the variation in the yield of product in response to the identity and amount of base used is quite similar for the cyclic tetramer and cyclic octamer, as would be expected if the cyclic octamer is a precursor to the cyclic tetramer. In separate experiments starting with pure samples of *p*-*tert*-butylcalix[8]arene as well as *p*-*tert*-butylcalix[6]arene we have demonstrated the conversion of these two cyclic oligomers to *p*-*tert*-butylcalix[4]arene by treatment with base in refluxing diphenyl ether, the rate of conversion for cyclic octamer being considerably greater than that for cyclic hexamer.[9] The slower rate of conversion from cyclic hexamer may provide an explanation for the increased time requred to obtain cyclic tetramer from the reaction employing 0.05 equiv of KOH (see Table II), because higher base concentrations and larger cations are known to be conducive to cyclic hexamer formation.[7] The mechanistic implications of these observations along with studies related to cyclic hexamer formation will be discussed in other papers.

Experimental Section

***p*-*tert*-Butylcalix[4]arene without Neutralization of the Precursor.** To a 1-L Erlenmeyer flask were added 100 g (0.665 mol) of *p*-*tert*-butylphenol, 62.3 mL of 37% formalin (0.83 mol of HCHO), and 1.2 g (0.03 mol) of NaOH (corresponding to 0.045 equiv of the phenol) dissolved in a minimum amount of H_2O. The contents of the flask were heated (oil bath) for 1.5–2 h, maintaining the temperature of the bath 110–120 °C. During this period the reaction mixture which was clear in the beginning became viscous and turned orange at first and then changed to a thick yellow mass. At this point the flask was removed from the heating bath and allowed to cool to room temperature, and the contents (referred to as the precursor) were removed and broken into small pieces. The precursor (which can also be made directly in a three-necked flask) was then suspended in 800–1000 mL of diphenyl ether in a 2-L three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and condenser. The contents of the flask were heated with a glas-col heater. During the first phase of the reaction, as the yellow precursor went into solution, the condenser was left off of the setup and nitrogen was blown rapidly over the reaction mixture to facilitate the removal of the water that evolved. When the water evolution subsided and when a precipitate started

(8) Buriks, R. S.; Fauke, A. R.; Munch, J. H. U.S. Patent 4 259 464, filed 1976, issued 1981.

(9) Lin, L.-g., unpublished observations.

Table III. Effect of the Identity of the Base on the Yield of *p-tert*-Butylcalix[8]arene

base	equiv of base	crude product yield, %	crude product mp, °C	recrystallized product yield, %	recrystallized product mp, °C
LiOH	0.01	31	395	23	405
	0.02	31	393	25	404
	0.03	33	384	27	401
	0.04	45	393	35	400
	0.05	39	389	31	405
NaOH	0.01	46	353	39	401
	0.02	51	349	46	400
	0.03	68	344	53	405
	0.04	63	345	53	400
	0.05	74	340	57	401
KOH	0.01	19	375	15	402
	0.02	65	349	55	399
	0.03	60	350	48	399
	0.04	77	349	55	396
	0.05	74	348	51	397
RbOH	0.01	54	349	33	401
	0.02	38	350	23	402
	0.03	66	352	35	402
	0.04	68	351	37	399
	0.05	68	351	36	398

to form, prior to attaining the reflux temperature, the condenser was put in place and the contents of the flask were refluxed for 1.5–2 h. During this phase of the reaction the initial precipitate disappeared to give a clear solution. The reaction mixture was then cooled to room temperature, treated with 1 L of ethyl acetate, stirred for 15–30 min, and allowed to stand for 30 min. Filtration yields material which was washed twice with 100 mL of ethyl acetate and once with 200mL of acetic acid to yield 66.5 g (62%) of crude product. Recrystallization from toluene gave 61.6 g of product as glistening white plates, mp 342–344 °C (reported[7] mp 344–346 °C), corresponding to a 50% yield if it is assumed that the product is a 1:1 complex with toluene.

***p-tert*-Butylcalix[4]arene with Neutralization of the Precursor.** To a 250-mL Erlenmeyer flask were added 25 g (0.166 mol) of *p-tert*-butylphenol, 18 mL (0.24 mol) of 37% formaldehyde solution, and 0.265 g (0.0066 mol) of NaOH (corresponding to 0.040 equiv). The reaction was carried on as described above, and the precursor was isolated and dissolved in chloroform. The chloroform solution was washed several times with aqueous HCl to completely remove all of the NaOH from the precursor and then with water. Evaporation of the chloroform yielded the neutral precursor which was added to diphenyl ether, along with the appropriate amount of base, and the remainder of the reaction was carried out as described above.

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Registry No. *p-tert*-Butylcalix[4]arene, 60705-62-6; *p-tert*-butylphenol, 98-54-4; *p-tert*-butylcalix[6]arene, 78092-53-2; *p-tert*-butylcalix[8]arene, 68971-82-4.

Cyclization of Trimethylsilyl-Substituted α-Allenic Alcohols to 3-(Trimethylsilyl)-2,5-dihydrofurans and Their Facile Autoxidation to 3-(Trimethylsilyl)furans or 4-(Trimethylsilyl)-2(5*H*)-furanones

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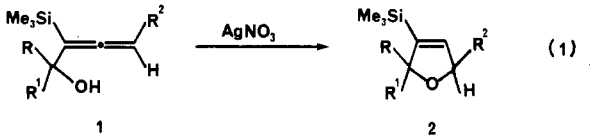
Trimethylsilyl-substituted dihydrofurans and furans have found useful synthetic applications. Recently, it was reported that 3-(trimethylsilyl)-2,5-dihydrofurans on epoxidation and subsequent treatment with sulfuric acid were smoothly converted to furans.[1] Epoxidation of furans has also been directed toward the double bond bearing an electron-releasing trimethylsilyl group to afford the corresponding butenolides regioselectively.[2] These observations have aroused considerable interest in this area.[3]

One synthetic route to 2,5-dihydrofurans is by silver(I)-catalyzed cyclization of α-allenic alcohols.[4] We recently described a simple method for the preparation of a variety of trimethylsilyl-substituted α-allenic alcohols.[5] Treatment of these compounds with silver nitrate under a nitrogen atmosphere thus provided the corresponding 3-(trimethylsilyl)-2,5-dihydrofurans (eq 1). The results are summarized in Table I.



1 2 (1)

In the case of **1f**, a small amount of an α,β-unsaturated ketone, 3-ethyl-4-(trimethylsilyl)-3-nonen-5-one (10%), was also isolated. Presumably, the tertiary carbocation **3f** was first produced followed by the attack of water at the central carbon of the allenyl system (eq 2). The trimethylsilyl group may have further stabilized the β-carbocationic intermediate **3f** through hyperconjugation.[6]

Table I. Preparation of 3-(Trimethylsilyl)-2,5-dihydrofurans

compd	R	R^1	isolated yield of 2,[a,b] %
1a	H	C_6H_5	65
1b	H	CH_3	53
1c	H	i-C_3H_7	72
1d	H	n-C_5H_{11}	60
1e		$-(CH_2)_5-$	54
1f	C_2H_5	C_2H_5	42[c]

[a] R^2 = n-C_3H_7. [b] The isolated yields (5-mmol reaction) are uncorrected for the presence of ca. 10–15% of β-acetylenic alcohols in the starting materials. In the case of **1f**, 3-ethyl-4-(trimethylsilyl)-3-nonen-5-one (10%) was also isolated. [c] 2.5-mmol reaction.

Table II. Formation of α-(Trimethylsilyl)-α,β-unsaturated Ketones

compd	R	R^1	R^2	isolated yield of 4,[a] %
1g	CH_3	CH_3	n-C_3H_7	36[b]
1h	CH_3	CH_3	H	48
1i		$-(CH_2)_5-$	H	24

[a] 5-mmol reaction unless otherwise indicated. [b] 2.5-mmol reaction.

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