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

		crude product		recrystallized product	
base	equiv of base	yield, %	mp, °C	yield, %	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.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work through an Industry/University Cooperative Research grant (CHE-8216719).

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]

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]

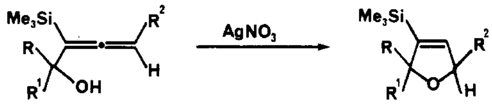
[a] $R^2 = n$-C_3H_7. [b] The isolated yields (5-mmol reaction) are uncorrected for the presence of ca. 10–15% of β-acetylenic alcohols in the starting materials. In the case of **1f**, 3-ethyl-4-(trimethylsilyl)-3-nonen-5-one (10%) was also isolated. [c] 2.5-mmol reaction.

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.

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]

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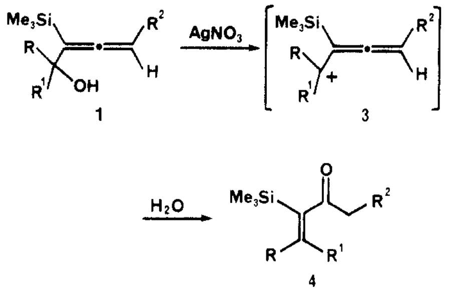
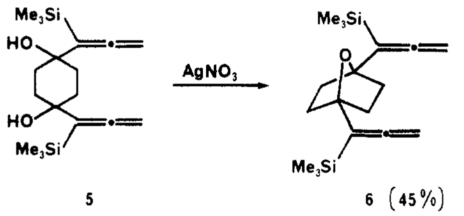


(2)

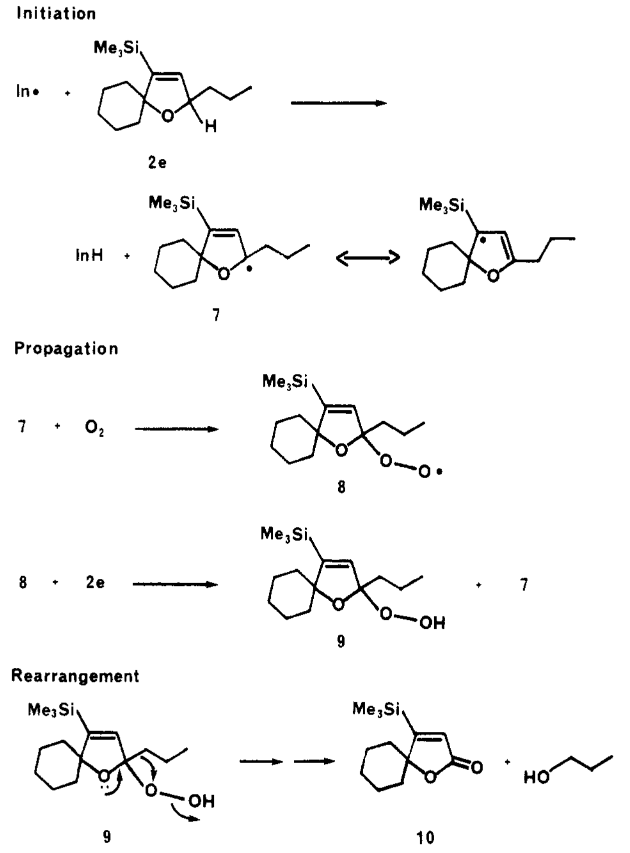
Attempts to cyclize the α-allenic alcohols in Table II resulted in the isolation of α-(trimethylsilyl)-α,β-unsaturated ketones **4**[7] in low to modest yields. Unidentified high boiling adducts were also obtained on further elution of the silica gel column with diethyl ether. Presumably, the sterically less hindered tertiary alcohol **1g** made the formation of the carbocation **3g** more favorable and thus provided **4g** and other undesirable byproducts. In both **1h** and **1i**, the terminal allenic structure may discourage the formation of a partial positive charge through complexation with silver ion at the terminal primary carbon atom for cyclization. Indeed, we were able to trap the carbocationic intermediate internally by a hydroxyl group in **5** to form **6** (eq 3). Such a change of the reaction pathway due to the variation of the substituents on the allenyl system as well as on the carbon atom bearing the hydroxyl group has been observed previously in the reactions of α-allenic alcohols with acids.[8]



(3)

The dihydrofurans in Table I were found to be very sensitive to air oxidation. In fact, when cyclization of **1b** was carried out under air, only 2-methyl-3-(trimethylsilyl)-5-propylfuran was isolated. In the case of **1e** also, dihydrofuran was not obtained. Instead, we were surprised by the isolation of spirolactone **10**. A proposed mechanism to account for its formation is given in Scheme I. Autoxidation of ethers by a free-radical chain mechanism to yield hydroperoxides is a facile process.[9] The reaction rate may be further enhanced by the ability of silicon to stabilize an α-radical through vicinal (d-p)π overlap,[10] thus greatly facilitating the formation of intermediate **7**. The hydroperoxide **9** then proceeds through a Baeyer–Villiger-type rearrangement to spirolactone **10** and 1-propanol. Such a rearrangement of 2-hydroperoxy-2,5-dihydrofurans derived from cyclobutadiene ozonides has been proposed as a possible reaction pathway to account for the formation of γ-lactones in the addition of singlet oxygen to 2-(methoxymethyl)furans.[11] The isolated dihydrofuran **2e** (colorless liquid) on standing in air was cleanly oxidized to **10** (crystalline solid) in less than 72 h, and 1-propanol was also detected by a GC/MS spectrometer.

Scheme I



In summary, various types of 3-trimethylsilyl-substituted 2,5-dihydrofurans and furans have been readily prepared to be used for further synthetic elaborations. The presence of the trimethylsilyl group may provide a handle for introducing functional groups at the less accessible 3-position of the furan ring. The effects of the trimethylsilyl group on the reactions of dihydrofurans and furans may also be of theoretical interests.

Experimental Section

The trimethylsilyl-substituted α-allenic alcohols were prepared as described previously.[5] ^{1}H and ^{13}C NMR spectra were recorded on a Varian EM-360 (60 MHz in ^{1}H) and a Varian CFT-20 (20 MHz in ^{13}C) spectrometer, respectively ($CDCl_3$, Me_4Si). IR spectra were taken on a Beckman IR8 spectrometer. Mass spectra were obtained on a Finnigan 4021 GC/MS instrument. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN.

3-(Trimethylsilyl)-2-phenyl-5-propyl-2,5-dihydrofuran (2a). The following procedure is representative for the cyclization of trimethylsilyl-substituted α-allenic alcohols. To a 50-mL round-bottomed flask equipped with a refluxing condenser and a magnetic stirring bar was added 0.850 g (5 mmol) of silver nitrate. The flask was then flushed with nitrogen, and 10 mL of an acetone/water (1:1) mixture was introduced via syringe. To the mixture was added 1.30 g (5 mmol) of 1-phenyl-2-(trimethylsilyl)-2,3-heptadiene (**1a**) via a syringe and the solution was heated to reflux for 48 h. After extraction with ethyl ether (3 × 50 mL), the combined organic layer was washed with water (4 × 20 mL), dried (anhydrous $MgSO_4$), and concentrated to give a dark oily residue. Column chromatography of the residue (silica gel, 60–80 °C petroleum ether) afforded 0.840 g (65% yield) of **2a** as a colorless liquid: IR (neat) 1600 (C=C), 1245, 835, 750, 695 cm^{-1}; ^{1}H NMR δ 7.23 (s, 5 H), 6.05 (d, 1 H, $J = 2$ Hz), 5.72 (dd, 1 H, $J = 2$ and 4 Hz), 4.82 (m, 1 H), 1.55 (br, 4 H), 0.9 (t, 3 H), −0.15 (s, 9 H); ^{13}C NMR δ 143.9, 142.3, 140.0, 128.2, 127.9, 92.5, 87.0, 38.9, 19.2, 14.2, −1.5; MS, m/e 260 (M$^+$). Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.74; H, 9.42. The ^{13}C

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NMR spectrum suggests the presence of only one *dl* pair.

2-Methyl-3-(trimethylsilyl)-5-propyl-2,5-dihydrofuran (2b): colorless liquid; IR (neat) 1600 (C=C), 1250, 1125, 835, 750, 690 cm^{-1}; ^{1}H NMR δ 6.0 (br, 1 H), 5.2–4.6 (m, 2 H), 1.5 (br, 4 H), 1.33 (d, 3 H, J = 6 Hz), 0.95 (t, 3 H), 0.13 (s, 9 H); ^{13}C NMR δ 144.6, 139.6, 86.4, 86.0, 39.2, 23.7, 18.8, 14.2, –1.1; MS, *m/e* 198 (M$^+$).

2-Methyl-3-(trimethylsilyl)-5-propylfuran (0.248 g, 51% yield) was obtained when the cyclization reaction of **1b** (0.495 g, 2.5 mmol) was carried out under air. The product (colorless liquid) had the following: IR (neat) 1555, 1250, 1200, 835, 750, 690 cm^{-1}; ^{1}H NMR δ 5.9 (s, 1 H), 2.52 (t, 2 H, J = 7 Hz), 2.26 (s, 3 H), 1.9–1.3 (m, 2 H), 0.93 (t, 3 H), 0.17 (s, 9 H).

2-Isopropyl-3-(trimethylsilyl)-5-propyl-2,5-dihydrofuran (2c): colorless liquid; IR (neat) 1600 (C=C), 1250, 1030, 885, 830, 750, 690 cm^{-1}; ^{1}H NMR δ 6.0 (br, 1 H), 4.9–4.5 (m, 2 H), 2.0–1.2 (m, 5 H), 1.1–0.8 (br, 3 H), 1.06 (d, 3 H, J = 7 Hz), 0.75 (d, 3 H, J = 7 Hz), 0.13 (s, 9 H); ^{13}C NMR δ 142.2, 140.7, 94.9, 86.4, 38.3, 31.7, 20.8, 19.3, 15.5, 14.3, –1.1; MS, *m/e* 226 (M$^+$).

3-(Trimethylsilyl)-2-pentyl-5-propyl-2,5-dihydrofuran (2d): colorless liquid; IR (neat) 1600 (C=C), 1250, 835, 750, 690 cm^{-1}; ^{1}H NMR δ 5.97 (br, 1 H), 5.1–4.5 (br, 2 H), 1.80–1.13 (br, 12 H), 0.92 (br, 6 H), 0.13 (s, 9 H); ^{13}C NMR δ 143.3, 140.0, 90.0, 86.4, 39.1, 37.0, 32.0, 25.3, 22.7, 19.0, 14.2, 14.1, –1.0. The column on further elution gave 3-(trimethylsilyl)-2-pentyl-5-propylfuran (0.101 g, 8% yield). This air oxidized adduct was not observed by GLC before column chromatography. The product had the following: colorless liquid: IR (neat) 1550, 1245, 835, 755, 690 cm^{-1}; ^{1}H NMR δ 5.86 (s, 1 H), 2.53 (t, 6 H, J = 7 Hz), 1.89–1.18 (br, 8 H), 1.1–0.8 (m, 6 H), 0.2 (s, 9 H).

2,2-Pentamethylene-3-(trimethylsilyl)-5-propyl-2,5-dihydrofuran (2e): colorless liquid; IR (neat) 1595, 1250, 830, 755, 690 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.95 (d, 1 H, J = 1 Hz), 4.97–4.63 (br, 1 H), 2.00–1.30 (br, 14 H), 0.93 (br, 3 H), 0.13 (s, 9 H); ^{13}C NMR (C_6D_6) δ 148.2, 140.8, 93.2, 84.6, 39.5, 39.3, 37.3, 26.1, 23.2, 22.9, 19.4, 14.5, –0.04; MS, *m/e* 252 (M$^+$). Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.36; H, 11.22.

2,2-Diethyl-3-(trimethylsilyl)-5-propyl-2,5-dihydrofuran (2f): colorless liquid; IR (neat) 1595, 1455, 1250, 1145, 1080, 995, 950, 835, 750, 690 cm^{-1}; ^{1}H NMR δ 6.1 (d, 1 H, J = 2 Hz), 4.7 (br, 1 H), 1.8–1.3 (br, 8 H), 0.85 (t, 9 H), 0.13 (s, 9 H). The column on further elution with petroleum ether/ether (98:2) gave 3-ethyl-4-(trimethylsilyl)-3-nonen-5-one (0.058 g, 10% yield of a 2.5-mmol reaction) as a colorless liquid: IR (neat) 1685 (s, C=O), 1600 (C=C), 1250, 1145, 1070, 1015, 835, 755, 690 cm^{-1}; ^{1}H NMR δ 2.50–1.24 (m, 10 H), 0.94 (t, 9 H), 0.07 (s, 9 H).

2-Methyl-3-(trimethylsilyl)-2-octen-4-one (4g). The product was isolated by using a mixture of petroleum ether and ether (98:2) as eluent. The product had the following: colorless liquid; IR (neat) 1685 (C=O), 1615 (C=C), 1250, 1150, 835, 755, 690 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.3 (t, 2 H), 1.75 (s, 3 H), 1.62 (s, 3 H), 1.6–1.1 (br, 4 H), 0.85 (t, 3 H), 0.12 (s, 9 H); ^{13}C NMR δ 212.8, 144.5, 142.8, 44.5, 25.4, 24.0, 23.6, 22.5, 14.0, 0.0. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.73; H, 11.28.

2-Methyl-3-(trimethylsilyl)-2-penten-4-one (4h): colorless liquid: IR (neat) 1680 (C=O), 1610 (C=C), 1250, 1190, 900, 835, 750, 685 cm^{-1}; ^{1}H NMR δ 2.15 (s, 3 H), 1.83 (s, 3 H), 1.72 (s, 3 H), 0.18 (s, 9 H); ^{13}C NMR δ 210.9, 144.2, 143.1, 32.1, 24.0, 23.5, –0.07; MS, *m/e* 170 (M$^+$). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.70; H, 10.46.

1,1-Pentamethylene-2-(trimethylsilyl)-1-buten-3-one (4i): colorless liquid; IR (neat) 1680 (C=O), 1610 (C=C), 1350, 1250, 1185, 835, 755, 690cm^{-1}; ^{1}H NMR δ 2.16 (s, 3 H), 2.1 (br, 4 H), 1.55 (br, 6 H), 0.16 (s, 9 H); ^{13}C NMR δ 210.9, 152.1, 139.3, 34.6, 34.3, 32.7, 28.4, 26.1, 0.1.

1,4-Bis[1-(trimethylsilyl)-1,2-propadienyl]-1,4-cyclohexanediol (5) was prepared from 1,4-cyclohexanedione by using the procedure described previously.[5] A white solid (1.443 g, 86% yield of a 10-mmol reaction) was obtained after column chromatography (silica gel, 98:2 petroleum ether/ether). The product had the following: mp 35 °C; IR (melt) 3530 (OH), 1930 (C=C=C), 1445, 1360, 1315, 1240, 980, 860, 835, 815, 755, 685 cm^{-1}; ^{1}H NMR δ 4.45 (s, 4 H), 2.2–1.3 (m, 10 H), 0.18 (s, 18 H); ^{13}C NMR δ 207.2, 106.3, 72.4, 71.8, 34.4, 0.6.

1,4-Bis[1-(trimethylsilyl)-1,2-propadienyl]-7-oxabicyclo[2.2.1]heptane (6) (0.374 g, 45% yield of a 2.5-mmol reaction) was isolated by column chromatography (silica gel, 98:2 petroleum ether/ether) as a white solid: mp 40–42 °C; IR (melt) 1930 (C=C=C), 1250, 1185, 1060, 990, 970, 880, 840, 755, 690 cm^{-1}; ^{1}H NMR δ 4.35 (s, 4 H), 1.65 (s, 8 H), 0.15 (s, 18 H); ^{13}C NMR δ 208.7, 98.6, 85.9, 69.9, 37.5, –0.01; MS, *m/e* 318 (M$^+$). Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.86; H, 9.49. Found: C, 67.83; H, 9.68.

5,5-Pentamethylene-4-(trimethylsilyl)-2(5*H*)-furanone (10) (0.281 g, 50% yield) was obtained from **1e** (0.625 g, 2.5 mmol) by carrying out the cyclization reaction under air. The product had the following: white crystalline solid (mp 108–110 °C); IR (KBr) 1735 (s, C=O), 1440, 1270, 1245, 1210, 1130, 985, 955, 935, 900, 880, 870, 830, 755, 735, 690 cm^{-1}; ^{1}H NMR δ 6.32 (s, 1 H), 2.1–1.5 (br, 10 H), 0.3 (s, 9 H); ^{13}C NMR δ 178.7, 172.4 128.7, 93.1, 35.2, 24.8, 22.3, –0.9; MS, *m/e* 224 (M$^+$). Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 64.62; H, 8.98. The spirolactone **10** was also obtained by placing dihydrofuran **2e** (0.356 g) in a 10-mL flask with periodic opening of the stopper to allow air oxidation. Within 72 h, 0.258 g (82% yield) of **10** was isolated as a crystalline solid after recrystallization from 60–80 °C petroleum ether. The liquid in the flask before recrystallization was found to contain 1-propanol by a GC/MS spectrometer.

Acknowledgment. We thank Professor William R. Moore for helpful discussions. Financial support by the National Science Foundation is gratefully acknowledged.

Registry No. 1a, 87655-84-3; **1b**, 99947-98-5; **1c**, 87655-82-1; **1d**, 87655-80-9; **1e**, 87655-90-1; **1f**, 87655-88-7; **1g**, 87655-86-5; **1h**, 79015-65-9; **1i**, 79015-67-1; **2a**, 99947-99-6; **2b**, 99948-00-2; **2c**, 99948-01-3; **2d**, 99948-02-4; **2e**, 99948-03-5; **2f**, 99948-04-6; **4g**, 99948-06-8; **4h**, 99948-07-9; **4i**, 99948-08-0; **5**, 99948-09-1; **6**, 99948-10-4; **10**, 99948-11-5; $AgNO_3$, 7783-99-5; 3-ethyl-4-(trimethylsilyl)-3-nonen-5-one, 99948-05-7; 2-methyl-3-(trimethylsilyl)-5-propylfuran, 86918-01-6; 3-(trimethylsilyl)-2-pentyl-5-propylfuran, 99965-47-6.

Kinetics of Some Methylenecyclopropane Rearrangements

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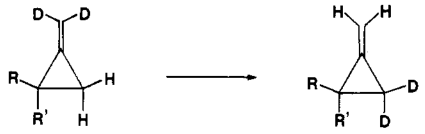
Received October 4, 1985

In pursuing our work on the thermolysis of 4-methylene-1-pyrazolines[1] we required information relating to the degenerate rearrangement of methylenecyclopropane and methyl-substituted methylenecyclopropanes. Gilbert[2a] had earlier observed a facile degenerate rearrangement at 52 °C of **1a** ⇄ **2a**, and our products, **1b** and **2b**, were observed to be slowly interconverting under the conditions required to thermolyze the pyrazoline reactants.



1 2

a $R = R' = C_6H_5$
b $R = R' = CH_3$
c $R = R' = H$
d $R = H$; $R' = CD_2{=}CD$

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