proceeds cleanly at room temperature to produce the acetic acid derivative in good yield, demonstrating further the general compatibility of the $Fe(CO)_3$ protecting unit with common reagents and sequences.[11] Alternatively, the sulfonylated adduct can be treated with a further equivalent of sodium hydride and another equivalent of electrophile, such as a different dienyl iron cation, giving unsymmetrical diarylacetic acid precursors by a tandem arylation process.

The sequences so far examined are given in Scheme I.[12]

A recent paper[13] reports the conversion of a malonate adduct of a similar cyclohexadienyliron cation to the corresponding acetate as proceeding in 51% yield. The present method should therefore allow for some improvement in this result.

Experimental Section

General Procedures. Melting points were obtained on a Kofler hot-stage apparatus and are uncorrected. IR samples were measured on a Perkin-Elmer 257 spectrometer with deuteriochloroform as the solvent. Matched sodium chloride cells were used for this purpose. NMR spectra were recorded on a Varian HA-100 spectrometer with deuteriochloroform containing 1% tetramethylsilane as the solvent. Mass spectra were obtained on an AE1 MS902 spectrometer operating at 70 eV. Tetrahydrofuran (THF) was dried prior to use by distillation from sodium–benzophenone ketyl. Methanol was dried by distillation from magnesium in the presence of iodine. Tricarbonylcyclohexadienyliron salts 1 and 2 were prepared by literature procedures.[14,15] The anion of methyl (phenylsulfonyl)acetate was prepared in THF by using a stoichiometric quantity of sodium hydride as the base. Complete deprotonation required 15 min at room temperature.

Procedure for Alkylation of Salts 1 and 2. By use of typical syringe techniques, a THF solution of methyl sodio(phenylsulfonyl)acetate (5.5 mmol) was added dropwise to a stirred suspension of the cation salt 1 or 2 (1.97 g, 5 mmol) in THF (20 mL) at 0 °C. After being stirred for 15 min the homogeneous solution was poured into water and then extracted with ether in the usual way. After being dried ($MgSO_4$), the organic phase was evaporated to leave a yellow oil which was chromatographed on silica gel with toluene–ethyl acetate (9:1) as the eluent. Isolation of the yellow band gave 3 or 4 as mixtures of diastereomers. By this process (methoxycyclohexadienyl)iron salt 1 gave sulfone 3 as an oil, 1.37 g (59%). A single diastereomer crystallized from methanol: mp 115–125 °C; NMR δ 7.94–7.42 (m, 5 H), 5 .16 (dd, J = 6, 2 Hz, 1 H), 3.87 (d, J = 7 Hz, 1 H), 3.60 (s, 3 H), 3.57 (d, J = 2 Hz, 1 H), 3.48 (s, 3 H), 3.18–2.54 (m, 2 H), 2.1–1.42 (m, 2 H); IR ν_{max} 2055, 1980, 1740 cm^{-1}; mass spectrum, m/e 462 (M^+). Anal. Calcd for $C_{19}H_{18}FeO_8S$: C, 49.4; H, 3.9. Found: C, 49.4; H, 4.1.

Likewise, salt 2 gave sulfone 4 as an oil, 1.93 g (83%). A single diastereomer crystallized from hexane: mp 140–155 °C; NMR δ 7.9–7.44 (m, 5 H), 4.98 (dd, J = 6, 2 Hz, 1 H), 3.61 (s, 3 H), 3.59 (s, 3 H), 3.52 (d, J = 7 Hz, 1 H), 3.38 (m, 1 H), 2.18 (dd, J = 6, 3 Hz, 1 H), 2.13 (m, 2 H), 1.27 (br s, 1 H); IR ν_{max} 2042, 1975, 1735 cm^{-1}; mass spectrum, m/e 462 (M^+). Anal. Calcd for $C_{19}H_{18}FeO_8S$: C, 49.4; H, 3.9. Found: C, 49.2; H, 4.0. A sample crystallized from MeOH (mp 135–145 °C) was shown by NMR to consist of a mixture of diastereomers.

Sulfonated adduct 4 (0.23 g, 0.5 mmol) was treated with NaH (0.5 mmol, room temperature, 15 min), and the resultant clear solution was added to a slurry of unsubstituted cyclohexadienyliron salt (1, R = R^1 = H; 0.5 mmol) in the manner just described. Chromatography over silica gel gave 7 initially as an oil which crystallized from hexane: 0.2 g (59%); mp 85–125 °C; the NMR of this material showed the expected structural features although the spectrum was complicated by the presence of diastereomers; IR ν_{max} 2045, 1975, 1735 cm^{-1}; mass spectrum, m/e 680 (M^+), together with six successive losses of CO. These data support structure 7.

Desulfonation Procedure. Sodium amalgam 5%, (2.7 g) was added in three portions over 30-min period to a stirred suspension of anhydrous sodium monohydrogen phosphate (0.28 g, 2 mmol) in dry MeOH (15 mL) containing the sulfonated complex 3 or 4 (0.23 g, 0.5 mmol). TLC (toluene–SiO_2) after this time indicated disappearance of the starting material and formation of one, faster running material. The mixture was decanted into water and then extracted with ether. A yellow oil was obtained after drying and concentration of the organic phase. Chromatography (toluene–SiO_2) gave the desulfonated complex as a yellow oil. In this manner sulfone 3 gave acetic ester 5: 0.13 g (81%); NMR δ 5.16 (dd, J = 6, 2 Hz, 1 H), 3.63 (s, 3 H), 3.60 (s, 3 H), 3.36 (m, 1 H), 2.5 (m, 1 H), 2.42–2.10 (m, 3 H), 1.94 (m, 1 H), 1.18 (br d, J = 16 Hz, 1 H); IR ν_{max} 2050, 1975, 1730 cm^{-1}; mass spectrum, m/e 322 (M^+). Anal. Calcd for $C_{13}H_{14}FeO_6$: C, 47.9; H, 5.6. Found: C, 47.8; H, 5.6.

By a similar process 4 gave 6 (R = R^2 = OMe; R^1 = R^2 = OMe; R^1 = H): 0.144 (90%); NMR δ 5.02 (dd, J = 6, 2 Hz, 1 H), 3.57 (s, 6 H), 3.23 (m, 1 H), 2.63 (dd, J = 7, 3 Hz, 1 H), 2.4–1.9 (m, 4 H), 1.39 (br d, J = 16 Hz, 1 H); IR ν_{max} 2045, 1975, 1735 cm^{-1}; mass spectrum, m/e 322 (M^+). Satisfactory combustion values were not obtained in this case. However, saponification of the ester with KOH/MeOH gave a yellow solid (88%), shown to be the corresponding acid 6: mp 103–105 °C; NMR δ 10.95 (s, 1 H) and 3.6 (s, 3 H) were the only features that differed from the spectrum of the ester (see above); IR ν_{max} 2045, 1970, 1700 cm^{-1}; mass spectrum, m/e 308 (M^+). Anal. Calcd for $C_{12}H_{12}FeO_6$: C, 46.8; H, 3.9. Found: C, 46.5; H, 4.1.

Acknowledgment. It is a pleasure to acknowledge Professor A. J. Birch, under whose direction this work was carried out.

Registry No. 1, 74883-20-8; 1 (R = R^1 = H), 42535-11-5; 2, 51508-59-9; 3, 81857-44-5; 4, 81857-45-6; 5, 81857-46-7; 6, 81857-47-8; 6 (R = R^2 = OMe; R^1 = H), 81857-48-9; 7, 81875-68-5.

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(12) The yields quoted refer to pure, isolated materials. All complexes gave satisfactory ^1H NMR, IR, and mass spectra, as well as combustion values. The mass spectral fragmentations of the sulfonyl-containing complexes 3 and 4 differed from the usual patterns observed in that a peak for M – 28 was in relatively low abundance. In the adduct related to 4 having a Me group at position 5, the mass spectrum shows a disproportionate relative abundance of the M – 56 fragment.

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Catalysts for Silylations with 1,1,1,3,3,3-Hexamethyldisilazane

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Received December 2, 1981

Trimethylsilylation of organic compounds having labile hydrogen atoms finds increasing use in analytical and in preparative organic chemistry.[1] Several methods have become available for silylation of alcohols, mercaptans, carboxylic acids, amides, heterocyclic nitrogen compounds, etc., using a variety of silylating agents.[2]

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The use of some silylating agents is limited by their unavailability or the laborious processes of purifying the products. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is a commercially available, cheap reagent,[1] giving ammonia as the only byproduct, and, generally speaking, products are separated from any excess of HMDS used by simple techniques. However, its poor silylating power[2a] is a main drawback.

Reactions with phthalimide[3] and tertiary alcohols[4] do not take place and the forceful conditions required in many other instances limit its use. Accordingly, several procedures have been developed to catalyze silylations with HMDS, using, for example, chlorotrimethylsilane,[4] bromotrimethylsilane,[5] sulfonic acids,[6] trifluoroacetic acid,[7] amine and ammonium salts,[8] and imidazole[3] as catalysts. Although these procedures provide an improvement, in many cases reaction times of several hours are still necessary. We report a new class of very effective catalysts[9] for silylations with HMDS that are of the general formula XNHY, in which at least one of X and Y is an electron-withdrawing group containing a CO, SO_2, or OP=moiety directly linked to the nitrogen atom and the other may be hydrogen, or X and Y together represent such an electron-withdrawing group, forming a cyclic system with the nitrogen atom. These catalysts, examples of which are to be found in Tables II and III, are applied in concentrations of 0.001–10 mol % and may be added to the reaction mixture as the sodium or trimethylsilyl derivative.

Application of these catalysts causes silylations of many classes or organic compounds to proceed with considerably increased rate. Tertiary alcohols and phthalimide react smoothly.

Compounds that were trimethylsilylated in this way are alcohols, phenols, carboxylic acids, hydroxamic acids, carboxylic amides and thioamides, sulfonamides, phosphoric amides, mono- and dialkyl phosphites, mercaptans, hydrazines, amines, NH groups in heteroaromatic rings, and enolizable β-diketones; yields are usually better than 90%.

Contrary to literature data,[10,11] silylations of carboxylic and thiocarboxylic acids result in clear solutions, so obviously no ammonium salts are present at the end of the reaction; consequently, products can simply be distilled from the reaction mixture. Furthermore, *N,O*-bis(trimethylsilyl) derivatives of 6-aminopenicillanic and 7-aminodeacetoxycephalosporanic acid derivatives, which can only be obtained with difficulty by other methods,[12] were prepared in good yield in refluxing chloroform.

It is noteworthy that saccharin, a useful catalyst, can only be silylated with HMDS in the presence of a more potent catalyst (see the Experimental Section). We consider this catalytic method a useful extension of the application of HMDS in both protective silylation and the preparation of well-known and potential silylating agents.

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Experimental Section

Commercially available starting materials were used without prior purification, unless otherwise stated. HMDS was carefully fractionated and of at least 98% purity. Melting points were determined in capillary tubes and are uncorrected; similarly, all boiling points recorded are uncorrected. ^1H NMR spectra were recorded on a JEOL C60HL spectrometer; chemical shifts are reported relative to tetramethylsilane (δ = 0) used as an internal standard. ^{13}C NMR spectra were taken on a Varian CFT20 instrument, using an internal solvent deuterium lock. Chemical shifts are quoted on the δ scale with respect to tetramethylsilane. Yields were not optimized. Yields of more than 98.5% are reported as quantitative. Because of the instability of many of the silylated products, elemental analyses were avoided.

General Procedure. Substrate and catalyst were mixed with the appropriate solvent, if any, and the mixture was heated to the reflux temperature or the temperature mentioned. A stream of dry nitrogen was passed over the mixture to ensure anhydrous conditions and to expel the ammonia generated in the reaction. HMDS was dropped in as quickly as possible (usually within 5 min), depending on the vigorousness of the reaction. Reaction times were determined by passing the nitrogen stream through water and titrating the ammonia absorbed, of which more than 95% of the calculated amount was recovered in all cases. Reaction times are recorded from the beginning of the addition of HMDS. The results are summarized in Table I.

Comparison of the Activity of Catalysts. A. 1-Hexanol (5.10 g, 50 mmol) was mixed with one of the catalysts mentioned in Table II and placed in an oil bath of 130 °C. HMDS (7.8 mL, 37.5 mmol) was added and the ammonia evolved was titrated with 1 N H_2SO_4 as described in the General Procedure. The time (t) in which half of the theoretical amount of ammonia was absorbed was taken as a measure for the catalytic activity. Further details are to be found in Table II.

B. By the same procedure, times (t) were measured for the reactions of 1.48 g (20 mmol) of 1-butanol in 10 mL of refluxing dichloromethane with 2.50 mL (12 mmol) of HMDS, using the catalysts listed in Table III.

17β-[(Trimethylsilyl)oxy]-4-androsten-2-one. Hexamethyldisilazane (246 mg, 1.5 mmol) was added to a refluxing suspension of 577 mg (1.99 mmol) of 17β-hydroxy-4-androsten-2-one and 1.8 mg (0.01 mmol) of saccharin in 10 mL of dichloromethane. The course of the reaction was followed by means of thin-layer chromatography (Kieselgel 60 F254, Merck A.G., Darmstadt; eluent, toluene–acetone, 9:1). After the mixture was refluxed for 2 h, starting material could no longer be detected and a single spot (R_f 0.47) had been formed. Evaporation to dryness yielded 0.68 g (95%) of 17β-[(trimethylsilyl)oxy]-4-androsten-2-one, mp 126–128 °C dec (lit.[13] mp 130–132 °C).

Trimethylsilyl 7-[(Trimethylsilyl)amino]-3-[[(1-methyl-1*H*-tetrazol-5-yl)thio]methyl]-3-cephem-4-carboxylate. Following the general procedure above, 1.64 g of 7-amino-3-[[(1-methyl-1*H*-tetrazol-5-yl)thio]methyl]-3-cephem-4-carboxylic acid of 91% purity (4.6 mmol) was silylated by being refluxed for 2 h in 30 mL of chloroform with 3.0 mL (14.4 mmol) of HMDS, using 5.0 mg (0.01 mmol) of bis(4-nitrophenyl) *N*-(trichloroacetyl)phosphoramidate as a catalyst. Evaporation to dryness, using a rotary evaporator, yielded a foam, which was dried in vacuo. A quantitative yield of trimethylsilyl 7-[(trimethylsilyl)amino]-3-[[(1-methyl-1*H*-tetrazol-5-yl)thio]methyl]-3-cephem-4-carboxylate was obtained: ^1H NMR (CCl_4) δ 0.11 (s, 9 H, $NSi(CH_3)_3$), 0.34 (s, 9 H, $COOSi(CH_3)_3$, 1.43 (d, 1 H, J = 12 Hz, NH), 3.66 (s, 2 H, SCH_2 in ring), 3.90 (s, 3 H, CH_3), 4.14 and 4.51 (AB q, 2 H, J = 13.5 Hz, CH_2S), 4.58 (d, J = 4.5 Hz), 4.83 (d, J = 4.5 Hz), 4.82 (s) together 2 H (β-lactam protons).

Trimethylsilylation of Saccharin. According to the method described in the General Procedure, HMDS (2 mL, 9.6 mmol) was added to 1.83 g (10 mmol) of saccharin and 10 mg (0.02 mmol) of bis(4-nitrophenyl) *N*-(4-toluenesulfonyl)phosphoramidate in 20 mL of acetonitrile. The calculated amount of ammonia was

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Table I. Preparation of Trimethylsilyl Derivatives

no.	substrate	molar ratio HMDS/ substrate	catalyst[a] (mol %)	solv or rctn temp, °C	rctn time, min	% yield[b]
1	C_6H_5COOH	0.75	A (0.50)	CH_2Cl_2	40	92
		0.75	B (0.50)	CH_2Cl_2	40	97
2	C_6H_5CSOH	0.75	D (0.25)	CH_2Cl_2	30	quant
3	$C_2H_5OOCCH_2COOH$	0.58	A (0.10)	CH_2Cl_2	90	97
4	*d,l*-$HOCH_2CH(NH_2)COOH$	2.5	A (0.50)	$C_6H_5CH_3$	180	76
5	$HSCH_2COOH$[c]	1.48	C (0.08)	$C_6H_5CH_3$	90	91
6	HS-C=N-N=N-N-CH_2COOH	1.29	D (0.65)	$ClCH_2CH_2Cl$	60	quant[d,e]
7	HS-C=N-N=N-N-CH_2COOH	1.45	A (1.50)	$C_6H_5CH_3$	120	quant[d,f]
8	O=C-$CH_2CH_2CH_2C$(=)CH_2	4.00	A (0.53)	130	50	81
9	*n*-$C_{12}H_{25}OH$	0.75	A (0.50)	130	15	98
10	$CH_3(CH_2)_3C(CH_3)_2OH$	0.75	C (0.10)	140	15	92
11	2-$CH_3C_6H_4OH$	0.75	A (0.50)	CH_2Cl_2	30	94
12	2,6-$[CH(CH_3)CH_2CH_3]_2C_6H_3OH$	0.75	E (0.10)	$CHCl_3$	210	90
13	$C_6H_{12}O_6$ (fructose)	5.00	A (1.00)	$CHCl_3$-C_5H_5N (3:1)	60	91
14	HO-N-C(O)CH_2CH_2CO	0.79	A (0.53)	130	15	87
15	C_6H_5SH	0.76	A (0.52)	$CHCl_3$	165	92
16	HS-C=N-N=C(CH_3)S	0.75	A (0.50)	$C_6H_5CH_3$	30	91[g]
17	CH_3CONH_2	0.75	A (0.30)	130	35	83
18	CH_3CSNH_2	0.55	A (0.50)	$C_6H_5CH_3$	90	59
19	4-$O_2NC_6H_4CONH_2$	0.70	A (0.90)	$CH_3COOC_4H_9$	15	quant[d]
20	H_2NCONH_2	1.20	A (1.00)	$CH_3COOC_2H_5$	20	quant[d]
21	$CH_3SO_2NH_2$	0.77	A (0.35)	$C_6H_5CH_3$	20	quant[d]
22	$C_6H_5SO_2NH_2$	0.75	A (1.00)	$CH_3COOC_2H_5$	25	quant[d]
23	4-$CH_3C_6H_4SO_2NHOH$	0.96	D (0.20)	CH_2Cl_2	50	quant[d,h]
24	4-$CH_3C_6H_4NH_2$	0.75	A (0.50)	130	120	83
25	$C_6H_5NHNH_2$	0.75	A (0.50)	130	120	90[i]
26	CH=CH-N=CH-N-H	0.75	A (0.08)	$C_6H_5CH_3$	50[j]	88
27	*o*-C_6H_4-CO-NH-CO	0.69	A (0.20)	120	60	quant[d]
28	$(C_2H_5O)_2POH$	1.38	D (0.14)	CH_2Cl_2	90	91
29	$[(C_6H_5O)_2PO_2]_2NH$	0.77	A (1.00)	$C_6H_5CH_3$	15	quant[d]
30	H_3PO_4	3.28	A (0.25)	CH_3CN	60	93

[a] A: saccharin; B: sodium saccharin; C: 4-$CH_3C_6H_4SO_2NHPO(OC_6H_4NO_2-4)_2$; D: $[(C_6H_5O)PO]_2NH$; E: $Cl_3CCONHPO(OC_6H_4NO_2$-4$)_2$. [b] Yield of distilled product, unless otherwise indicated. All groups with active hydrogen are silylated, unless otherwise stated; NH_2 groups are monosilylated. [c] Freshly distilled sample. [d] Yield obtained after evaporation of the reaction mixture. [e] Mp 130–133 °C; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 4.99 (s, 2 H), 14.3 (s, 1 H), only COOH silylated. [f] Oil; ^{1}H NMR (CCl_4) δ 0.29 (s, 9 H), 0.65 (s, 9 H), 4.87 (s, 2 H). [g] Bp 150–152 °C (15 torr); mp 67–69 °C; ^{1}H NMR (CCl_4) δ 0.57 (s, 9 H), 2.42 (s, 3 H). [h] Mp 87–90 °C; ^{1}H NMR (CCl_4) δ 0.17 (s, 9 H), 2.43 (s, 3 H), 6.90 (s, 1 H), 7.20, 7.34, 7.69, 7.83 (q, 4 H); product is the *O*-trimethylsilyl derivative. [i] Product is $C_6H_5NHNHSi(CH_3)_3$. [j] Vigorous reaction; HMDS added dropwise over 20 min.

Table II. Trimethylsilylation of 1-Hexanol

catalyst	mol %	*t*, min
none		22
succinimide	5.0	18
3,3-dimethylglutarimide	5.0	16
maleimide	5.0	9
1,8-naphthalimide	5.0	8
3,4,5,6-tetrachlorophthalimide	2.0	4
3,4,5,6-tetrabromophthalimide	2.0	4
barbituric acid	2.0	12
1,2-benzisothiazol-3(2*H*)-one	5.0	9
4-(benzoyloxy)-1,2-dihydro-1-oxophthalazine	5.0	7
saccharin	0.5	4
dimethyl *N*-(trichloroacetyl)phosphoramidate	0.1	7
bis(4-nitrophenyl) *N*-(trichloroacetyl)phosphoramidate	0.1	1.5
	0.01	3
bis(4-nitrophenyl) *N*-(4-toluenesulfonyl)phosphoramidate	0.1	1.5
	0.001	6
tetraphenyl imidodiphosphate	0.1	1
	0.001	13

generated in 30 min. After evaporation of the volatile materials, 2.50 g (98%) of trimethylsilylated saccharin was obtained. The

Table III. Trimethylsilylation of 1-Butanol

catalyst	mol %	*t*, min
none		42
bis(4-nitrophenyl) *N*-[(dimethylamino)sulfonyl]phosphoramidate	0.5	2
diisopropyl *N*-(dichloroacetyl)phosphoramidate	0.5	22
bis(2-chlorophenyl) *N*-[(4-chlorophenyl)sulfonyl]phosphoramidate	1.0	17
N,N-dimethylsulfamide	5.0	15
trimethylsilylated saccharin	0.1	4
N-(1-naphthoyl)-4-toluenesulfonamide	1.0	8
N-(2-methoxybenzoyl)-4-toluenesulfonamide	5.0	22

product (mp 90–92 °C) was approximately a 1:2 mixture of 2-(trimethylsilyl)-1,2-benzisothiazolin-3-one 1,1-dioxide and 3-[(trimethylsilyl)oxy]-1,2-benzisothiazole 1,1-dioxide: ^{1}H NMR (CCl_4) δ 0.53 and 0.57 (2 s, together 9 H), 7.66–8.13 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −1.2, −0.4, 1.8, 120.5, 121.4, 123.6, 124.8, 133.3, 133.8, 134.8.

Registry No. $C_6H_5COOSiMe_3$, 2078-12-8; $C_6H_5CSOSiMe_3$, 7528-43-0; $C_2H_5OOCCH_2COOSiMe_3$, 18457-03-9; *dl*-$Me_3SiOCH_2CH(NHSiMe_3)COOSiMe_3$, 64625-17-8; $(CH_3)_3SiSCH_2COOSi(CH_3)_3$, 6398-62-5; HS-(cyclo-C=N-N=N-N)-$CH_2COOSi(CH_3)_3$, 81589-11-9; n-$C_{12}H_{25}OSiMe_3$, 6221-88-1; $H_3C(CH_2)_3C(CH_3)_2OSiMe_3$, 81588-99-0; 2-$CH_3C_6H_4OSiMe_3$, 1009-02-5; 2,6-$[CH(CH_3)CH_2CH_3]_2C_6H_3OSiMe_3$, 61283-84-9; $C_6H_{12}O_6$(fructose)$[Si(CH_3)_3]_5$, 19126-98-8; Me_3SiO-(cyclo-N-C(O)CH_2CH_2CO), 74124-80-4; $C_6H_5SSi(CH_3)_3$, 4551-15-9; $(CH_3)_3SiS$-(cyclo-C=N-N=C(CH_3)S), 81589-00-6; $CH_3CONHSiMe_3$, 13435-12-6; $CH_3CSNHSiMe_3$, 58065-67-1; $4O_2NC_6H_4CONHSiMe_3$, 1020-48-0; $Me_3SiNHCONHSiMe_3$, 18297-63-7; $CH_3SO_2NHSiMe_3$, 999-96-2; $C_6H_5SO_2NHSiMe_3$, 17865-14-4; 4-$CH_3C_6H_4SO_2NHOSiMe_3$, 81974-63-2; 4-$CH_3C_6H_4NHSiMe_3$, 63911-83-1; $C_6H_5NHNHSiMe_3$, 13271-92-6; (cyclo-CH=CH-N=CH-N)-$SiMe_3$, 18156-74-6; o-(cyclo-C_6H_4-CO-N($SiMe_3$)-CO), 10416-67-8; $(C_2H_5O)_2POSiMe_3$, 13716-45-5; $(C_6H_5O)_2PONHSiMe_3$, 17938-28-2; $(SiMe_3)_3PO_4$, 10497-05-9; C_6H_5C-OOH, 65-85-0; C_6H_5CSOH, 98-91-9; $C_2H_5OOCCH_2COOH$, 1071-46-1; dl-$HOCH_2CH(NH_2)COOH$, 302-84-1; $HSCH_2COOH$, 68-11-1; HS-(cyclo-C=N-N-N-N)-CH_2CO_2H, 57658-36-3; n-$C_{12}H_{25}OH$, 112-53-8; $CH_3(CH_2)_3C(CH_3)_2OH$, 2370-12-9; 2-$CH_3C_6H_4$-OH, 95-48-7; 2,6-$[CH(CH_3)CH_2CH_3]_2C_6H_3OH$, 5510-99-6; $C_6H_{12}O_6$(fructose), 57-48-7; HO-(cyclo-N-C(O)CH_2CH_2CO), 6066-82-6; C_6H_5SH, 108-98-5; HS-(cyclo-C=N-N=C(CH_3)S), 29490-19-5; CH_3CONH_2, 60-35-5; CH_3CSNH_2, 62-55-5; 4-$O_2NC_6H_4CONH_2$, 619-80-7; H_2NCONH_2, 57-13-6; $CH_3SO_2NH_2$, 3144-09-0; $C_6H_5SO_2NH_2$, 98-10-2; 4-$CH_3C_6H_4SO_2NHOH$, 1593-60-8; 4-$CH_3C_6H_4NH_2$, 106-49-0; $C_6H_5NHNH_2$, 100-63-0; (cyclo-CH=CH-N=CH-NH), 288-32-4; o-(cyclo-C_6H_4CONHCO), 85-41-6; $(C_2H_5O)_2POH$, 868-85-9; $(C_6H_5O)_2PONH_2$, 2015-56-7; H_3PO_4, 7664-38-2; 4-$CH_3C_6H_4SO_2NHPO(OC_6H_4NO_2\text{-}4)_2$, 81589-21-1; $[(C_6H_5O)_2PO]_2NH$, 3848-53-1; $Cl_3CCONHPO(OC_6H_4NO_2\text{-}4)_2$, 38187-67-6; 1-hexanol, 111-27-3; 17β-hydroxy-4-androsten-2-one, 82639-21-2; 7-amino-3-[(1-methyl-1H-tetrazol-5-yl)thio]methyl]-3-cephem-4-carboxylic acid, 24209-38-9; 1-butanol, 71-36-3; 1-[(trimethylsilyl)oxy]hexane, 17888-62-9; 17β-[(trimethylsilyl)oxy]-4-androsten-2-one, 82639-22-3; trimethylsilyl 7-[(trimethylsilyl)amino]-3-[[1-methyl-1H-tetrazol-5-yl)thio]methyl]-3-cephem-4-carboxylate, 81589-17-5; 2-(trimethylsilyl)-1,2-benzisothiazolin-3-one 1,1-dioxide, 82639-23-4; 3-[(trimethylsilyl)oxy]-1,2-benzisothiazole 1,1-dioxide, 82639-24-5; hexamethyldisilazane, 999-97-3; saccharin, 81-07-2; sodium saccharin, 128-44-9; succinimide, 123-56-8; 3,3-dimethylglutarimide, 1194-33-8; maleimide, 541-59-3; 1,8-naphthalimide, 81-83-4; 3,4,5,6-tetrachlorophthalimide, 1571-13-7; 3,4,5,6-tetrabromophthalimide, 24407-32-7; barbituric acid, 67-52-7; 1,2-benzisothiazol-3(2H)-one, 2634-33-5; 4-(benzoyloxy)-1,2-dihydro-1-oxophthalazine, 1705-04-0; dimethyl N-(trichloroacetyl)phosphoramidate, 1666-45-1; bis(4-nitrophenyl) N-[(dimethylamino)sulfonyl]phosphoramidate, 81589-29-9; diisopropyl N-(dichloroacetyl)phosphoramidate, 3807-94-1; bis(2-chlorophenyl) N-[(4-chlorophenyl)sulfonyl]phosphoramidate, 81589-30-2; N,N-dimethylsulfonamide, 3984-14-3; N-(1-naphthoyl)-4-toluenesulfonamide, 81589-31-3; N-(2-methoxybenzoyl)-4-toluenesulfonamide, 81589-32-4.

Supplementary Material Available: Physical constants for the products of Table I and Table IV containing 30 additional examples (3 pages). Ordering information is given on any current masthead page.

Fragmentation of Bicyclo[4.4.1]undecan-11-ones

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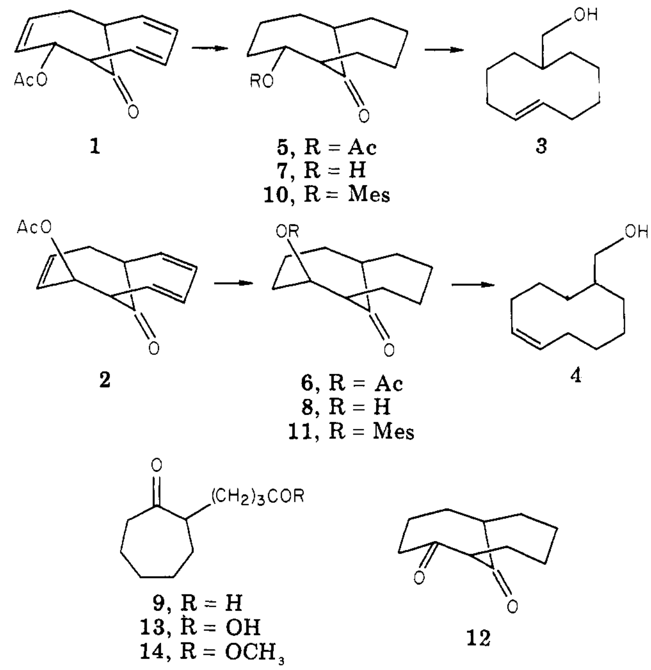
Received March 12, 1982

The formation of 8- to 12-membered rings remains a synthetic challenge because of entropy and enthalpy losses upon cyclization.[2] A common approach to these systems has been the fragmentation of the bicyclic structure, which requires that the bond being broken and the leaving group have an antiperiplanar relationship.[3] Bicyclo[4.4.0]decanes have been shown to fragment to yield either (E)- or (Z)-cyclodecenes.[4-6] One-carbon bridged systems have been used to generate Z isomers of cyclooctenes and cyclodecenes.[7] Herein we describe the fragmentation reactions of two isomeric bicyclo[4.4.1]undecanes **10** and **11** that afford (E)-cyclodecene **3** and (Z)-cyclodecene **4**, respectively, establishing that the fragmentation of an appropriate one-carbon bridge system can afford either olefin isomer.

Scheme I



1; **5**, R = Ac; **7**, R = H; **10**, R = Mes; **3**; **2**; **6**, R = Ac; **8**, R = H; **11**, R = Mes; **4**; **9**, R = H; **13**, R = OH; **14**, R = OCH_3; **12**

The formation of bicyclo[4.4.1]undecatrienones via the [6 + 4] cycloaddition reaction of cycloheptatrienones has been examined in detail.[8] The use of stereochemically pure dienes has permitted the selective formation of 7α-acetoxybicyclo[4.4.1]undeca-2,4,8-trien-11-one (**1**) and

(1) Undergraduate Research Participant, 1977, 1979; President's Summer Fellowship, 1978.

(2) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95–101.

(3) For recent application of this reaction and reviews, see Sternbach, D.; Shibuya, M.; Jaisli, F.; Bonetti, M.; Eschenmoser, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 634–637. Grob, C. A. *Ibid.* **1969**, *8*, 535–546. Grob, C. A.; Schiess, P. W. *Ibid.* **1967**, *6*, 1–15.

(4) For bicyclo[4.4.0]decane fragmentation stereochemistry, see Wharton, P. S.; Hiegel, G. A. *J. Org. Chem.* **1965**, *30*, 3254–3257.

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