Synthesis of Silyl and Germyl Ketones

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Abstract: Procedures for the synthesis of a number of silyl and germyl ketones, by hydrolysis of the related 2-substituted 1,3-dithianes, are given. New ketones described include several trialkylgermyl compounds, acetyltrimethylsilane, and new bisketones.

The study of the remarkable spectral properties of α-silyl and α-germyl ketones[1,2] has been severely restricted by the difficulties inherent in their synthesis. To date, only two general methods of synthesis have been employed—the hydrolysis, under mild conditions to avoid silicon–carbonyl carbon bond cleavage, of benzylic dibromides, prepared by dibromination of benzylsilanes with N-bromosuccinimide,[1,3] or the oxidation of α-silylcarbinols, a reaction occurring only in poor yield using conventional inorganic oxidizing agents but one which we have found quite successful using the dimethyl sulfoxide–carbodiimide reagent.[4,5] In this latter case, however, the unavailability of appropriate silylcarbinols restricts this as a general route to silyl ketones. The publication of the elegant new route to ketones *via* dithianes by Corey and Seebach[6] appeared to us to be a possible new general route to silyl and germyl ketones provided that relatively mild conditions for the hydrolysis of the dithianes could be found, and we immediately began synthesis of a number of typical compounds *via* the dithiane route. Corey and Seebach also recognized the potentiality of this method for the synthesis of sensitive and otherwise difficult to synthesize compounds, and among some typical examples investigated they recently reported[7] the synthesis of several silyl ketones which we were also investigating. In order to avoid unnecessary duplication of effort we agreed on the types of compound to be investigated by our respective research groups, and the following describes the results of our otherwise independent investigations initiated following the original Corey–Seebach publication.[6]

As illustrated in Table I, carbanions derived from 1,3-dithiane or 2-substituted 1,3-dithianes readily react with alkyl- or arylsilyl and -germyl halides. In general, conditions similar to those of Corey and Seebach were employed, metallation with *n*-butyllithium of the dithiane, usually in THF, but in a few cases in ether, being carried out for 1–3 hr at about −20° (Dry Ice–CCl_4 bath). The subsequent reaction of the carbanion with the halides was carried out by slow addition of the halide to the carbanion solution at about 0°, followed by from 1 to 18 hr further stirring at 0° or in some cases at room temperature (20°). Optimum conditions were not established in all cases. In a few cases two successive reactions with different halides were carried out without isolating the intermediate product, generally with yields comparable to those obtained from the single-step reactions, as noted by Corey and Seebach.

Hydrolysis of the various dithianes was attempted using a 3–5-fold excess of mercuric chloride, usually containing several equivalents of cadmium carbonate in aqueous solvents following the general procedure of Wolfrom, Konigsberg, and Weisblat.[8] By following the rate of CO_2 evolution from the reaction mixture, it was possible to get a qualitative idea of the rate of the hydrolysis. No detailed investigation of solvents was made but it appeared that acetone–benzene–water was preferable to acetone–tetrahydrofuran–water. For volatile ketones (*e.g.*, acetyltrimethylsilane) DMSO–H_2O was preferred because of the ease of isolation of the ketone which could be distilled out under reduced pressure, since difficulties were encountered in the ready separation of the ketone from large volumes of acetone and other organic solvents.

Table II lists the ketones prepared by hydrolysis of the dithianes. Of these (−)-acetyl-α-naphthylphenylmethylsilane and all four triethylgermyl ketones are new. Acetyltrimethylsilane, also previously unreported, was also prepared concurrently in these laboratories by another route. In general the synthesis of silyl and germyl ketones by the dithiane route is definitely the method of preference, since fewer steps involving the metalloid are involved, and these in general occur in better yield. Thus the synthesis of optically active benzoyl-α-naphthylphenylmethylsilane involved only two steps—reaction of the phenyldithiane carbanion with optically active silyl halide (78%), followed by hydrolysis (71%), to produce, without special precautions, asymmetric ketone which in one reaction had 100% optical purity, and in the second (larger) run had 95% optical purity. These two steps replace the sequence: asymmetric silyl chloride + benzylsodium (54%, but frequently not of high optical purity, and involving considerable experimental problems in handling the benzylsodium), dibromination of the benzylsilane (85%), and hydrolysis of the dibromide (80–85%). Since the absolute configurations of (−)-R_3Si^*Cl and (+)-R_3Si^*COPh are known to be different,[9] it is evident that attack of the dithiane

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(1) A. G. Brook, R. Kivisikk, and G. E. LeGrow, *Can. J. Chem.*, **43**, 1175 (1965), and references cited therein.

(2) A. G. Brook and G. J. D. Peddle, *J. Organometal. Chem.*, **5**, 106 (1966).

(3) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Am. Chem. Soc.*, **82**, 5102 (1960).

(4) A. G. Brook and J. B. Pierce, *J. Org. Chem.*, **30**, 2566 (1965).

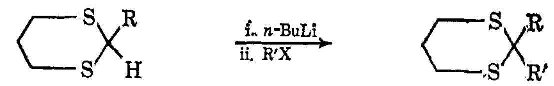
(5) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963).

(6) E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075, 1077 (1965).

(7) E. J. Corey, D. Seebach, and B. Erickson, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p 35K.

(8) M. L. Wolfrom, M. Konigsberg, and D. I. Weisblat, *J. Am. Chem. Soc.*, **61**, 574 (1935).

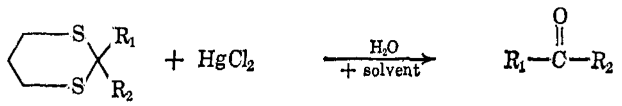
Table I. Silyl-, Germyl-, and Stannyl-1,3-dithianes



R	R'X	Yield,[a] %	Mp or bp (mm), °C
H	Me_3SiCl	70	100 (8), $n^{21}\mathrm{D}$ 1.5328
H	Ph_3SiCl	66[b]	174.5–176
CH_3	Me_3SiCl	95	94–96 (5)
Me_3Si	CH_3I	58[b]	94–96 (5), $n^{21}\mathrm{D}$ 1.5299
H	(a) Me_3SiCl, (b) MeI	62[c]	94–96 (5)
Ph_3Si	MeI	80	188–190
H	(a) Ph_3SiCl, (b) MeI	28	188–189
CH_3	(−)-α-NpPhMeSiCl	86	Undistilled, $[\alpha]^{20}\mathrm{D}$ 2.8° (c 12.2, C_6H_{12})
Ph	(−)-α-NpPhMeSiCl	78	167–163 from $MeOH–C_6H_6$, $[\alpha]^{20}\mathrm{D}$ 22.2° (c 7.1, $CHCl_3$)
Ph	Ph_3SiCl	66	199–200 from $MeOH–C_6H_6$
Ph_3Si	Ph_3SiCl	54	217 from $MeOH–C_6H_6$
H	Ph_3GeBr	77	172–173 from CCl_4
Ph_3Ge	MeI	64	182–183 from CCl_4
Me	Ph_3GeBr	60	182–183 from CCl_4
H	(a) Ph_3GeBr, (b) MeI	58	182–183 from CCl_4
H	Et_3GeBr	50	144 (3.5), $n^{22}\mathrm{D}$ 1.5440[22] (22)
H	(a) Et_3GeBr, (b) Et_3GeBr	17[b,d]	144 (0.15), $n^{22}\mathrm{D}$ 1.5447
Et_3Ge	MeI	63	104 (0.4), $n^{22}\mathrm{D}$ 1.5461
Me	Et_3GeBr	52	104 (0.4), $n^{20}\mathrm{D}$ 1.5461
Ph	Et_3GeBr	70	162 (0.3), $n^{20}\mathrm{D}$ 1.5920
Et_3Ge	Me_3SiCl	79	119 (0.5), $n^{20}\mathrm{D}$ 1.5491
H	Ph_3SnCl	79	149–150
CH_3	Ph_3SnCl	82	149.5–151.5
Ph	Ph_3SnCl	79	139–141 from $MeOH–C_6H_6$
H	$CH_2{=}CHCH_2CH_2Br$	49	83–86 (3), $n^{20}\mathrm{D}$ 1.5522
$CH_2{=}CHCH_2CH_2$	PhMeHSiCl	47	135–136 (0.03)[e]

[a] Reactions were run in THF unless otherwise mentioned. Metallations were carried out at about −20° and couplings with halides were carried out at 0° for the more reactive halides or at 20° for the less reactive or more highly sterically hindered systems. [b] Reaction solvent was ether. [c] Second step done in ether. Also isolated was 17% of 2,2-bis(trimethylsilyl)-1,3-dithiane. [d] 43% 2-triethylgermyl-1,3-dithiane also isolated. [e] Attempts to cyclize this compound by peroxide- or platinum-catalyzed Si–H addition to the double bond failed.

Table II. Ketones Generated from 1,3-Dithianes



R_1	R_2	Hydrolysis conditions	Yield, %	Physical properties
Me_3Si	CH_3	10% H_2O in DMSO,[a] 25°, 2 hr	69	Bp 113–114° (751 mm), $n^{20}\mathrm{D}$ 1.4113[f]
Ph_3Si	CH_3	2:1 acetone–benzene + 5% H_2O,[a] 25°, 1 hr	82	Mp 127–129°[b]
Ph_3Si	Ph	3:2 acetone–THF + 2% H_2O,[a] 17 hr, reflux	14	Mp 107–109°,[b] + 52% recovered dithiane
Ph_3Si	Ph	3:1 acetone–benzene + 5% H_2O,[a,e] 4.5 hr, reflux	69	Mp 108–109°[b]
(−)-α-NpPhMeSi	CH_3	2:1 acetone–benzene + 5% H_2O,[a] 1 hr, reflux	42	Mp 82.5–85°,[c] $[\alpha]^{20}\mathrm{D}$ −40.0° (c 8.33, C_6H_6)
(−)-α-NpPhMeSi	Ph	2:1 acetone–benzene + 5% H_2O,[a] 3 hr, reflux	71	Mp 82–84.5°,[b] $[\alpha]^{20}\mathrm{D}$ +6.05° (c 10.1, C_6H_6)
Ph_3Si	Ph_3Si	d		
Ph_3Ge	CH_3	10% H_2O in THF, 25°, 1.5 hr	58	Mp 122–123°[b,g]
Et_3Ge	Ph	10% H_2O in THF, 2 hr, reflux	63	Bp 82–83° (0.15 mm)
Et_3Ge	Me	10% H_2O in DMSO, 25°, 2 hr	54	Undistilled[h]
Et_3Ge	Et_3Ge	10% H_2O in MeOH–THF, 25°, 3 hr	. . .	Pink solution
Et_3Ge	Me_3Si	10% H_2O in MeOH–THF, 25°, 1.5 hr	. . .	Unstable pink solution

[a] $CdCO_3$ (4–5 mole equiv) present. [b] From EtOH. [c] From C_6H_{12}. [d] A variety of conditions, from 10% H_2O in MeOH with 5-hr reflux yielding 90% recovered dithiane, to 5-days reflux in 10% H_2O in THF, yielding 45% recovered dithiane, were used, but all failed to yield ketone. [e] $HgCl_2$ (15 mole equiv) used. [f] Characterized as the 2,4-dinitrophenylhydrazone, mp 140–141° from chloroform–hexane. *Anal.* Calcd for $C_{11}H_{16}SiN_4O_4$: C, 44.58; H, 5.44; N, 18.90. Found: C, 44.87; H, 4.91; N, 19.05. [g] Mixture melting point undepressed with sample provided by Dr. G. J. D. Peddle.[15] [h] Characterized as the 2,4-dinitrophenylhydrazone, mp 83.5–84.5° from petroleum ether (bp 60–70°). *Anal.* Calcd for $C_{14}H_{22}GeN_4O_4$: C, 43.90; H, 5.75; N, 14.63. Found: C, 43.80; H, 5.81; N, 14.56.

carbanion on the asymmetric silyl chloride has occurred stereoselectively with inversion of configuration, as has been observed consistently before[9-11] with other anions.

The dithiane route to metalloid ketones does, however, possess some limitations. Thus, although we have succeeded in preparing bistriphenylsilyl ketone by oxidation of the corresponding alcohol in reasonable yield,[2,12] we have failed to isolate any of this ketone from attempted hydrolysis of 2,2-bis(triphenylsilyl)-1,3-dithiane under a wide variety of conditions. On the other hand, unstable pink solutions containing ketone, as evidenced by their characteristic ultraviolet and infrared spectra, are readily obtained from bistriethylgermyldithiane and 2-triethylgermyl-2-trimethylsilyldithiane, but isolation of pure ketone from these systems has not yet been achieved. This inertness to hydrolysis of the bisarylsilyldithianes is reflected also in the monotriphenylsilyl-substituted dithianes which generally require much more vigorous hydrolysis conditions than their alkyl analogs. We regard this as an electronic rather than a steric effect. We have also been unsuccessful in isolating stannyl ketones in attempted hydrolyses of the stannyldithianes.

Prior to the preparation of acetyltrimethylsilane by the dithiane route, this compound was prepared in low yield[13] by oxidation of the mixture of trimethylsilylethanols produced by hydroboration followed by oxidation of trimethylvinylsilane. Seyferth[14] had reported that trimethylvinylsilane underwent hydroboration, leading to a significant amount of the abnormal isomer wherein the boron atom was attached to the secondary carbon atom, leading on oxidation to a significant amount of the secondary alcohol. Rather than attempt to separate the two trimethylsilylethanols, which appear to boil at about the same temperature, the mixture was oxidized with dicyclohexylcarbodiimide in dimethyl sulfoxide containing pyridinium trifluoroacetate following the method of Pfitzner and Moffatt,[5] and the ketone was then distilled in low yield from the mixture and purified by vpc. The ketone was characterized by its typical silyl ketone spectral properties (Table III) and by its nmr spectrum which consisted of two singlets with intensities in the ratio of 3:1 at δ = 0.18 and 2.20 ppm, respectively.

Table III reports the observed infrared and ultraviolet data for the new ketones. These are in complete accord with what has been observed already. Thus the infrared carbonyl band of acetyltrimethylsilane (6.08 μ, 1645 cm^{-1}) occurs at about the same wavelength as that of other alkylsilyl ketones (6.07–6.08 μ),[4] while the acetyl-[15] and benzoylgermanes[3] absorb at the expected wavelengths, somewhat lower than their silicon analogs. The new bisgermyl ketone absorbs at about the same wavelength as its phenyl analog.[2] The n–π^* transitions of the new ketones in the ultraviolet or visible regions are in accord with previous studies[1-4] and will not be discussed further here.

Table III. Spectral Data for Ketones

	Infrared, μ	Ultraviolet λ_{max}, mμ (ϵ)[a]
$Me_3SiCOCH_3$	6.08	In C_6H_{12}: 253 (50), 358 (100), 372(126), 387 (93)
$Et_3GeCOCH_3$	6.04	In C_6H_{12}: 314 (s) (15), 325 (s) (34), 340 (s) (76), 352 (129), 365 (173), 380 (143)
$Ph_3GeCOCH_3$	6.00	In C_6H_{12}: 260 (s) (1450), 265 (s) (1160), 271 (s) (743), 329 (s) (106), 341 (s) (186), 352 (298), 366 (385), 380 (310) mμ
$Et_3GeCOSiMe_3$		Unstable pink solution, in mixed MeOH–THF: 535
$Et_3GeCOPh$	6.14	In C_6H_{12}: 274 (s) (1100), 282 (s) (1050), 292 (s) (634), 409 (s) (131), 424 (151), 443 (s) (98)
$Et_3GeCOGeEt_3$	6.21	Unstable pink solution, in C_6H_6: 464, 495, 527

[a] (s) = shoulder.

Experimental Section[16]

Synthesis and Hydrolysis of Dithianes. 2-Triphenylsilyl-1,3-dithiane. To 5.7 g (0.0475 mole) of 1,3-dithiane in 120 ml of dry ether at −25° was added 0.05 mole of 1.25 *M n*-butyllithium in hexane over 11 min. After 1.5 hr Gilman Colour Test No. 2[17] was negative, indicating complete reaction of the butyllithium. The suspension was warmed to 0° and 14.7 g (0.05 mole) of triphenylchlorosilane in 75 ml of ether was added over 50 min. The resulting cloudy yellow solution was maintained at 0° for 3 hr. Work-up with 2% HCl gave some white precipitate which was removed and shown to be the desired compound. Work-up of the ether layer after drying gave an oil which on crystallization from benzene–methanol gave 11.85 g (66%) of white crystals, mp 175–177°.

2-Triethylgermyl-2-methyl-1,3-dithiane. To 10.0 g (0.745 mole) of 2-methyl-1,3-dithiane in 200 ml of anhydrous THF at −23° was added 60 ml of 1.25 *M n*-butyllithium (0.075 mole) in hexane. After stirring at −23° for 2 hr, the solution was warmed to 0° and 17.9 g (0.0745 mole) of triethylbromogermane in 50 ml of THF was added. After stirring at room temperature for 20 hr, work-up and distillation gave 11.4 g (52%) of 2-triethylgermyl-2-methyldithiane, bp 104° (0.4 mm).

Acetyltriphenylsilane. To 5.9 g (0.035 mole) of cadmium carbonate suspended in a solution of 4.65 g (0.015 mole) of mercuric chloride dissolved in 15 ml of acetone and 0.59 ml (0.033 mole) of water was added a solution of 1.18 g (0.003 mole) of 2-triphenylsilyl-2-methyl-1,3-dithiane in 25 ml of acetone and 10 ml of THF. The closed system was connected to a small bubbler and rapid gas evolution occurred over 15 min at 20°. After a total of 60 min, the acetone was removed from the viscous suspension under reduced pressure, and the white solid was washed thoroughly with chloroform, which was evaporated to dryness yielding 1.01 g (110%) of white solid, mp 122–125°. Recrystallization from ethanol gave 0.69 g (76%) of pure acetyltriphenylsilane, mp 126–128°, whose mixture melting point with an authentic sample[3,18] was not depressed. Use of acetone–benzene as the hydrolysis medium gave an 82% yield.

Benzoyltriethylgermane. A suspension of 10.0 g (0.028 mole) of 2-triethylgermyl-2-phenyl-1,3-dithiane, 38.5 g (0.142 mole) of mercuric chloride, and 24.6 g (0.143 mole) of cadmium carbonate in 90 ml of THF and 10 ml of water was refluxed overnight, gradually becoming yellow. The mixture was evaporated to dryness and

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(9) Studies by W. W. Limburg, published in part by A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

(10) A. G. Brook and C. M. Warner, *Tetrahedron Letters*, **18**, 815 (1962).

(11) L. H. Sommer "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, Chapter 4.

(12) Subsequent unpublished studies by P. Jones have given yields of 26%.

(13) Carried out by N. Davis, as an undergraduate research project, Jan–March 1966.

(14) D. Seyferth, *J. Am. Chem. Soc.*, **81**, 1844 (1959).

(15) G. J. D. Peddle, *J. Organometal. Chem.*, **5**, 486 (1966).

(16) Satisfactory analyses were obtained for all new compounds and are reported in Table IV.

(17) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

(18) Acetyltriphenylsilane has been prepared by G. E. LeGrow in yields of 40–50% by oxidation of 1-triphenylsilylethanol with chromic acid in aqueous acetone using the procedure described in ref 4 for propionyltriphenylsilane, or in 70–80% yield by use of the dimethyl sulfoxide–carbodiimide reagent described therein.

Table IV. Analyses of Compounds

R	R′	Formula	Calcd, %		Found, %	
			C	H	C	H
2-R-2-R′-1,3-Dithianes						
H	Me_3Si	$C_7H_{16}S_2Si$	43.70	8.38	43.66	8.37
H	Ph_3Si	$C_{22}H_{22}S_2Si$	69.78	5.86	70.69	5.66
CH_3	Me_3Si	$C_8H_{18}S_2Si$	46.54	8.79	46.55	8.68
Me_3Si	Me_3Si	$C_{10}H_{24}S_2Si$	45.39	9.14	46.67	9.14
CH_3	Ph_3Si	$C_{23}H_{24}S_2Si$	70.35	6.16	70.56	5.83
CH_3	α-NpPhMeSi	$C_{22}H_{24}S_2Si$	69.42	6.35	68.94	6.24
Ph	α-NpPhMeSi	$C_{27}H_{26}S_2Si$	73.25	5.92	73.67	6.10
Ph	Ph_3Si	$C_{28}H_{26}S_2Si$	73.96	5.76	73.71	5.70
Ph_3Si	Ph_3Si	$C_{40}H_{36}S_2Si$	75.51	5.66	74.67	5.63
H	Ph_3Ge	$C_{22}H_{22}GeS_2$	62.47	5.21	62.69	5.23
Me	Ph_3Ge	$C_{23}H_{24}GeS_2$	63.22	5.49	63.24	5.41
H	Et_3Ge	$C_{10}H_{22}GeS_2$	43.06	7.89	42.70	7.73
Et_3Ge	Et_3Ge	$C_{16}H_{36}Ge_2S_2$	43.91	8.23	45.38	8.38
Me	Et_3Ge	$C_{11}H_{24}GeS_2$	45.10	8.20	45.06	8.06
Ph	Et_3Ge	$C_{16}H_{26}GeS_2$	54.16	7.34	54.25	7.56
Et_3Ge	Me_3Si	$C_{13}H_{30}GeS_2Si$	44.46	8.55	44.76	8.32
H	Ph_3Sn	$C_{22}H_{22}S_2Sn$	56.31	4.73	56.99	4.92
Me	Ph_3Sn	$C_{23}H_{24}S_2Sn$	57.16	5.01	56.94	4.93
H	$CH_2{=}CHCH_2CH_2$	$C_8H_{14}S_2$	55.12	8.09	55.14	8.01
PhMeHSi	$CH_2{=}CHCH_2CH_2$	$C_{15}H_{22}S_2Si$	61.16	7.53	61.10	7.66
Ketones R—CO—R′						
CH_3	Me_3Si	$C_5H_{12}SiO$	51.66	10.41	51.66	10.71
CH_3	α-NpPhMeSi	$C_{19}H_{18}SiO$	78.57	6.25	78.72	6.26
Ph	Et_3Ge	$C_{13}H_{20}GeO$	58.95	7.56	58.28	7.46

thoroughly extracted with carbon tetrachloride. Evaporation of the solvent left 5.0 g (63%) of a viscous yellow oil, with carbonyl absorption at 6.14 μ. Distillation gave a clear yellow oil, bp 82–83° (0.15 mm).

Hydroboration of Vinyltrimethylsilane. To 800 ml of 1 *M* (0.8 mole) diborane in tetrahydrofuran[19] cooled in an ice bath was added 50 g (0.5 mole) of vinyltrimethylsilane with vigorous stirring. Stirring was continued over 18 hr at room temperature, and then, after cooling the reaction mixture to 0°, 50 ml of water was cautiously added, resulting in the precipitation of considerable white solid. Most of the tetrahydrofuran was removed under reduced pressure, and the precipitate (mainly boric acid) was thoroughly washed with methanol. The organoborane and methanol washings were neutralized with concentrated aqueous sodium hydroxide and then an additional 8.0 g (0.2 mole) of solid sodium hydroxide was added and dissolved by shaking. To the rapidly stirred mixture, 80 ml of 30% hydrogen peroxide (0.8 mole) was slowly added. After 1 hr stirring, water containing a little sodium chloride was added, and the mixture was thoroughly extracted with several portions of ether. The carbinol ether layers were back-extracted with dilute sodium chloride solution, and then were dried. Rough distillation gave a total of 24.2 g (41%) of mixed 1- and 2-trimethylsilylethanols, bp 60–75°, $n^{23}\text{D}$ 1.4200–1.4231.

Oxidation of Trimethylsilylethanol. To a solution of 4.1 g (0.0034 mole) of the above trimethylsilylethanol (estimated by vpc to contain 81% of the desired 1-trimethylsilylethanol) and 7.8 g (0.0034 mole) of pyridinium trifluoroacetate in 100 ml of dry dimethyl sulfoxide was added 14.5 g (0.0088 mole) of dicyclohexylcarbodiimide. The mixture, from which a large amount of white solid (dicyclohexylurea) precipitated, was stirred in the dark for 18 hr. After filtering off the solid, the solution was distilled at about 24 mm, and material boiling in the range 26–50° was collected in two Dry Ice traps. The distillate had very strong infrared absorption at 6.08 μ, and weaker absorption at 5.63 and 5.81 μ, probably due to small amounts of trifluoroacetic acid and an ester impurity. The distillate was taken up in ether and washed several times with water. The ketone was purified by vpc on an Aerograph Autoprep 70S instrument using a 6-ft SE 30 silicone gum rubber column, column temperature 80°, flow rate 300 ml/min, injection temperature 130°, elution time 34 min. It was identical in properties with the acetyltrimethylsilane prepared by the dithiane method, bp 113–114° (750 mm).

Acknowledgment. This research was supported by the National Research Council of Canada.

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[19] Supplied by Metal Hydrides Co., Beverley, Mass.

Synthesis of α-Silyl Ketones *via* 1,3-Dithianes

E. J. Corey, Dieter Seebach, and R. Freedman

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received September 2, 1966

Abstract: A new synthetic route to α-silyl ketones involving two steps from readily available components is described.

Recently we have described the generation of 2-lithio derivatives (**2**) from 1,3-dithianes (**1**) and the application of these nucleophilic reagents to the synthesis of a wide variety of organic compounds, including aldehydes, ketones, 1,*n*-diketones, α-hydroxy ketones, α-keto acids, and α-amino ketones.[1] The