chloride), 42833-66-9; **3** (R = Bu; n = 0), 57629-47-7; **3** (R = t-Bu; 3-MeO), 57598-43-3; **3** (R = t-Bu; 3-MeO) methiodide, 65000-02-4; **4** (R = t-Bu; 3-MeO), 57598-52-4; **5** (R = Bu; 2-MeO), 64957-90-0; **6** (R = Bu; 2-MeO), 20359-54-0; **9**, 57598-48-8; **10** (HCl), 64957-91-1; **13**, 64957-92-2; **13** (meta analogue), 64957-93-3; **14**, 38197-35-2; **15**, 64957-94-4; **16**, 64957-71-7; **17**, 64957-72-8; **23**, 64957-73-9; **24**, 65000-03-5; **27**, 64957-74-0; **28**, 64957-75-1; **29**, 64957-76-2; thionyl chloride, 7719-09-7; 2-amino-2-methyl-1-propanol, 124-68-5; 3-bromo(N-methyl-N-Boc)aniline, 57598-34-2; 2-p-bromophenyl-4,4-dimethyloxazol-2-ine, 32664-14-5; 2-o-bromophenyl-4,4-dimethyloxazol-2-ine, 32664-13-4; hexamethyldisilane, 1450-14-2; 1,4-dibromobutane, 110-52-1; p-dibromobenzene, 106-37-6; bromobenzene, 108-86-1; 6-bromo-1-hexene, 2695-47-8; 2-methoxyvalerophenone 2,4-DNP, 64957-70-6.

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(23) Professor D. J. Cram (UCLA) informed us that the addition of a large excess of phenylmagnesium bromide to **1d** gave the *m*-terphenyl derivative **27** in quantitative yield.

Sulfenylation and Sulfinylation of Lactams and Imino Ethers

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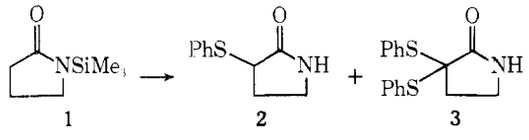
The sulfenylation of 1-trimethylsilyl-2-pyrrolidinone (**1**) with phenyl disulfide under a variety of reaction conditions afforded the bissulfide **3** as the major product along with the monosulfide **2**. The direct sulfinylation of **1** with methyl benzenesulfinate, however, could be achieved to afford the sulfoxide **4**. An analogous sulfinylation of 1-methyl-2-pyrrolidinone gave the sulfoxide **13** in excellent yield. The imino ether **5** could be monosulfenylated effectively by employing a 1:2:1 ratio of lactam/base/electrophile. It was also observed that in the sulfenylation of the N-alkyllactams **7** and **8** that HMPA had no effect on promoting bissulfenylation and that the ratio of substrate/base/electrophile is very important.

Recently, we reported[2] that mono- or bissulfenylation or selenenylation of N-methyllactams can be cleanly controlled by varying the equivalents of base utilized in the reaction. It has also been demonstrated[3] that an α-phenylselenenyl or an α-phenylsulfenyl moiety can be used to introduce a $\Delta^{3,4}$ double bond in an intact 2-pyrrolidinone nucleus.

In order to develop a synthetic sequence that would be compatible with the formation of a 3-pyrrolin-2-one system and also allow modification on the nitrogen, we were interested in utilizing the trimethylsilyllactam **1**[4] and the imino ether **5**. The results of the sulfenylation of **1** and **5** and related lactam chemistry are reported herein.

Reaction of the trimethylsilyllactam **1** with 2 equiv of LDA in THF at −78°C followed by sulfenylation with 1 equiv of phenyl disulfide and subsequent cleavage of the N–Si bond on workup afforded the monosulfide **2** in 29% yield and the

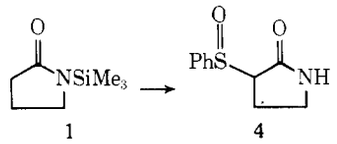


1 2 3

bissulfide **3** in 50% yield. When a 1:2:2 ratio of lactam/base/electrophile was employed, it was found that sulfenylation of **1** gave the bissulfide **3** in 84% yield along with 3% of the monosulfide **2**.

The best yield of the monosulfide was realized when a 1:1:2 ratio of lactam/base/electrophile was used with inverse quenching at 0 °C. In this case, **2** was obtained in a 35% yield and **3** in 33% yield. The results observed by varying the ratio of lactam/base/electrophile with or without the presence of HMPA and with or without inverse quenching are summarized in Table I.

Although the above results with respect to controlling mono- vs. bissulfenylation in the case of silylated lactams were discouraging, the problem could be circumvented, since it was found that sulfinylation of **1** with methyl benzenesulfinate[5]



1 4

could be achieved to afford the desired sulfoxide directly. Thus, reaction of **1** with 2 equiv of LDA in THF at −78 °C and subsequent sulfinylation with methyl benzenesulfinate (45 min at −78 °C and room temperature for 2 h) afforded a 67% yield of the crystalline sulfoxide **4**.

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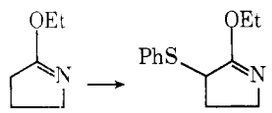
Table I. Sulfenylation of a Trimethylsilyllactam 1

Ratio of lactam/base/electrophile[a]	Equiv of HMPA	Yield, %[b] Mono-2	Bis-3
1:1:1	1	26	44
1:1:1[c,d]	1	20	39
1:1:2[c,e]		35	33
1:2:1		29	50
1:2:1[c,f]		20	55
1:2:2		3	84

[a] PhSSPh. [b] Isolated by column chromatography using silica gel G. [c] Inverse quenching. [d] 35 min at 0 °C and 0.5 h at room temperature. [e] 0 °C for 1.5 h and room temperature for 0.5 h. [f] −40 °C, 1.0 h.

The imino ether **5** can be envisioned as a synthon for the elaboration of the 2-pyrrolidinone nucleus and it also lends itself readily for modification on nitrogen. The bissulfenylation of the imino ether, 2-methoxy-3,4,5,6-tetrahydropyridine, has been reported by Trost and Kunz.[6] We were interested to ascertain if the imino ether **5** could be monosulfenylated under our conditions previously reported[2] for the sulfenylation of lactams, since monosulfenylation is a necessary requirement for the introduction of a $\Delta^{3,4}$ double bond in an intact 2-pyrrolidinone nucleus.

Reaction of the imino ether **5** with 2 equiv of LDA in THF



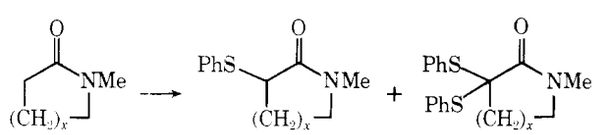
5 **6**

at −78 °C followed by sulfenylation with phenyl disulfide at −78 °C and subsequent warming to −20 °C and then to room temperature afforded a 46% yield of the distilled phenyl sulfide **6**.[7] No bissulfide was detected in this reaction.

Trost and co-workers[8] have shown that in THF solutions bissulfenylation of ketone enolates with phenyl disulfide does not occur regardless of the amount of excess base or disulfide, whereas bissulfenylation in THF–HMPA mixtures can occur. It has also been pointed out by these workers that HMPA effectively increases the rate of sulfenylation. In our earlier work[2] on the sulfenylation of α-methylenelactams in THF–HMPA solutions, it was observed that the ratio of substrate/base/electrophile was critical in controlled mono- vs. bissulfenylation. We therefore were interested in carrying out these sulfenylation reactions in THF alone to determine what role HMPA might have with respect to mono- and bissulfenylation.

These results using different ratios of base and electrophile are summarized in Table II. It appears in this case that HMPA has no effect on promoting bisulfenylation and that the ratio of base to disulfide is very important. Without the utilization of HMPA in these reactions, the purification of the products is much less laborous.

We have also observed that the lactam **7** can be sulfinylated



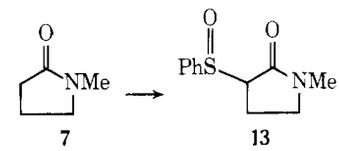
7, x = 1 **9**, x = 1 **11**, x = 1
8, x = 2 **10**, x = 2 **12**, x = 2

in high yield directly with methyl benzenesulfinate,[5] thus circumventing the problems association with bissulfenylation. Reaction of **7** with 2 equiv of LDA in THF at −78 °C and subsequent sulfinylation with methyl benzenesulfinate at −78 °C for 1 h, warming to room temperature, and stirring overnight afforded the crystalline sulfoxide **13** in 94% yield.

Table II. Sulfenylation of *N*-Methyllactams in THF

Substrate	Ratio of lactam/base/electrophile[a]	Compd (yield, %)[b] Mono	Bis
2	1:2:1	**9** (54)	**11** (2)
8	1:2:1	**10** (77)	**12** (0)
7	1:2:2	**9** (6)	**11** (83)
8	1:2:2	**10** (15)	**12** (62)
8	1:2:2[c]	**10** (0)	**12** (76)[d]

[a] PhSSPh. [b] Isolated by column chromatography using silica gel G. [c] Inverse quenching. [d] Isolated by direct crystallization.



7 **13**

Experimental Section

3-Phenylthio-2-pyrrolidinone (2) and 3,3-Diphenylthio-2-pyrrolidinone (3). General Procedure A. A 100-mL three-neck flask fitted with a nitrogen inlet tube, addition funnel, serum cap, and magnetic stirring bar was flamed and deaerated with nitrogen. A solution of diisopropylamine (5.15 g, 0.051 mol) in 30 mL of dry THF was added under N_2, and the reaction vessel was cooled to 0 °C. A hexane solution of 2.4 M *n*-butyllithium (21.23 mL, 0.051 mol) was added with a hypodermic syringe and allowed to stir at 0 °C for 10 min. The reaction mixture was then cooled to −78 °C with a dry ice–acetone bath, and 1-trimethylsilyl-2-pyrrolidinone (4.0 g, 0.0255 mol) dissolved in 10 mL of dry THF was added over a 5-min period. The reaction was allowed to stir at −78 °C for 35 min. Phenyl disulfide (5.55 g, 0.0255 mol) dissolved in 10 mL of THF was added dropwise over a 5-min period, and the addition funnel was then rinsed with 3 mL of THF. The reaction mixture was stirred for an additional 35 min at −78 °C. The reaction was allowed to warm to −20 °C, stirred at −20 °C for 20 min, and then allowed to warm to room temperature. The reaction mixture was poured into 400 mL of H_2O and extracted with three 350-mL portions of ether. The ether extracts were combined and washed consecutively with 150 mL of a 10% NaOH solution, 150 mL of H_2O, 150 mL of a 10% HCl solution, and 150 mL of H_2O. The ether solution was dried over anhydrous $MgSO_4$, filtered, and concentrated on a rotary evaporator, affording 6.0 g of an oil. The oil was chromatographed on silica gel G and elution with ether–hexane solutions gave 1.9 g (50%) of 3,3-diphenylthio-2-pyrrolidinone (**3**) [mp 100.5–102 °C (Et_2O trituration); NMR ($CDCl_3$) δ 7.92 (s, br, NH, 1 H), 7.10–7.84 (m, 10 H), 3.06 (t, 2 H), and 2.28 (t, 2 H); IR ($CHCl_3$) 3435, 3220, and 1700 (broad) cm^{-1}] and 1.4 g (29%) of 3-phenylthio-2-pyrrolidinone (**2**) [mp 120–120.7 °C (Et_2O–hexane trituration); NMR ($CHCl_3$) δ 7.95 (s, br, NH, 1 H), 7.14–7.75 (m, 5 H), 3.82 (t, 1 H), 3.27 (t, 2 H), and 1.80–2.86 (m, 2 H); IR ($CHCl_3$) 3435, 3224, and 1695 cm^{-1}].

Anal. Calcd for $C_{16}H_{15}NOS_2$: C, 63.76; H, 5.02; N, 4.65. Found: C, 63.72; H, 5.11 N, 4.61.

Anal. Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.09; H, 5.78; N, 7.24.

3-Phenylthio-2-pyrrolidinone (2) and 3,3-Diphenylthio-2-pyrrolidinone (3). General Procedure B. Inverse Quenching. A 50-mL three-neck flask fitted with an addition funnel, serum cap, and magnetic stirring bar was connected via a glass siphoning tube to a second 100-mL three-neck flask fitted with a nitrogen inlet tube, stopper, and magnetic stirring bar. The apparatus was flamed and deaerated with nitrogen. Phenyl disulfide (5.55 g, 0.0255 mol) dissolved in 20 mL of dry THF was placed in the 100-mL flask. A solution of diisopropylamine (1.29 g, 0.0128 mol) dissolved in 12 mL of THF was placed under nitrogen in the 50 mL-flask and cooled to 0 °C. A hexane solution of 2.4 M *n*-butyllithium (5.31 mL, 0.01274 mol) was added with a hypodermic syringe and allowed to stir at 0 °C for 10 min. The reaction mixture was cooled to −78 °C and 1-trimethylsilyl-2-pyrrolidinone (2.0 g, 0.01274 mol) dissolved in 7 mL of THF was added over a 5-min period. The reaction mixture was stirred for an

additional 0.5 h at −78 °C. The enolate solution was then siphoned through the glass tube into the solution of phenyl disulfide cooled to 0 °C. The resulting reaction mixture was stirred at 0 °C for 1.5 h and then at room temperature for 0.5 h. The reaction mixture was poured into 200 mL of H_2O and extracted with three 175-mL portions of ether. The ether extracts were combined and washed consecutively with 75 mL of a 10% NaOH solution, 75 mL of H_2O, 75 mL of a 10% HCl solution, and 75 mL of H_2O. The ether solution was dried over anhydrous $MgSO_4$ and filtered, and concentration on a rotary evaporator afforded 3.2 g of an oil. The oil was chromatographed on silica gel G, and elution with ether–hexane solutions yielded 630 mg (33%) of 3,3-diphenylthio-2-pyrrolidinone (**3**) and 850 mg (35%) of 3-phenylthio-2-pyrrolidinone (**2**). The NMR and TLC analyses of compounds **2** and **3** were consistent when compared with those of authentic **2** and **3**.

3-Phenylthio-2-pyrrolidinone (2) and 3,3-Diphenylthio-2-pyrrolidinone (3). A 1:1:1 Ratio with HMPA. Following the general procedure A, the amide enolate (0.01274 mol) was prepared in the usual way in 10 mL of dry THF. The reaction mixture was stirred at −78 °C for 10 min. Phenyl disulfide (2.78 g, 0.01274 mol) dissolved in 10 mL of THF containing HMPA (2.28 g, 0.01274 mol) was added over a 10-min period, and the reaction mixture was stirred at −78 °C for 35 min. The reaction mixture was allowed to warm to −20 °C, stirred at −20 °C for 20 min, and then allowed to warm to room temperature.

Workup as usual yielded an oil. The oil was chromatographed on silica gel G, and elution with ether–hexane solutions afforded 840 mg (44%) of **3** and 650 mg (26%) of **2**. The NMR and TLC analyses of compounds **2** and **3** were consistent when compared with those of authentic **2** and **3**.

3-Phenylthio-2-pyrrolidinone (2) and 3,3-Diphenylthio-2-pyrrolidinone (3). Inverse Quenching. A 1:1:1 Ratio with HMPA. Following the general procedure B, the amide enolate (0.01274 mol) was prepared in the usual way in 10 mL of dry THF. The reaction was stirred at −78 °C for 30 min. The enolate solution was then siphoned through a glass tube into a solution of phenyl disulfide (2.78 g, 0.01274 mol) dissolved in 10 mL of THF containing HMPA (2.28 g, 0.01274 mol) at 0 °C. The reaction was stirred at 0 °C for 35 min and then at room temperature for an additional 0.5 h.

Workup as usual yielded an oil. The oil was chromatographed on silica gel G and elution with ether–hexane solutions afforded 750 mg (39%) of **3** and 500 mg (20%) of **2**. The NMR and TLC analyses of compounds **2** and **3** were consistent when compared with those of authentic **2** and **3**.

3-Phenylthio-2-pyrrolidinone (2) and 3,3-Diphenylthio-2-pyrrolidinone (3). Inverse Quenching. A 1:2:1 Ratio. Following the general procedure B, the amide enolate (0.00637 mol) was prepared in the presence of LDA (0.01274 mol) in the usual way in 5 mL of THF. The reaction mixture was stirred at −78 °C for 10 min. The enolate solution was then siphoned through a glass tube into a solution of phenyl disulfide (1.39 g 0.00637 mol) dissolved in 10 mL of THF at −40 °C. The resulting reaction mixture was stirred at −40 °C for 1 h.

Workup as usual yielded an oil. The oil was chromatographed on silica gel G and elution with ether–hexane solutions afforded 525 mg (55%) of **3** and 245 mg (20%) of **2**. The NMR and TLC analysis of compounds **2** and **3** were consistent when compared with those of authentic **2** and **3**.

3-Phenylthio-2-pyrrolidinone (2) and 3,3-Diphenylthio-2-pyrrolidinone (3). A 1:2:2 Ratio. Following the general procedure A, the amide enolate (0.00637 mol) was prepared in the presence of LDA (0.0127 mol) in the usual way in 5 mL of THF. The reaction mixture was stirred at −78 °C for 35 min. Phenyl disulfide (2.77 g, 0.0127 mol) dissolved in 10 mL of THF was added dropwise over a 10-min period, and the reaction mixture was stirred at −78 °C for 35 min. The reaction mixture was allowed to warm to −20 °C, stirred at −20 °C (CCl_4–dry ice bath) for 20 min, and then allowed to warm to room temperature over a 40-min period. Workup as usual yielded an oil. The oil was chromatographed on silica gel G and elution with ether–hexane solutions afforded 1.6 g (84%) of **3** and 0.03 g (3%) of **2**. The NMR and TLC analyses of compound **3** were consistent when compared with those of authentic **3**.

3-Phenylsulfinyl-2-pyrrolidinone (4). Following the general procedure A, LDA (0.0446 mol) was prepared in the usual way in 10 mL of THF. The reaction mixture was cooled to −78 °C and 1-trimethylsilyl-2-pyrrolidinone (3.5 g, 0.0223 mol) dissolved in 15 mL of THF was added over a 10-min period. The reaction mixture was allowed to stir at −78 °C for 45 min, then allowed to come to room temperature, and stirred for 2 h.

The reaction was poured into 100 mL of a 10% sodium bicarbonate solution and extracted with three 350-mL portions of $CHCl_3$. The chloroform extracts were combined, washed with a dilute solution of HCl and a saturated NaCl solution, dried over anhydrous $MgSO_4$, and filtered, and concentration on a rotary evaporator afforded a brown oil. The oil was chromatographed on silica gel G, and elution with ether–methanol solutions afforded 3.1 g (67%) of **4** as a white solid: NMR ($CDCl_3$) δ 7.05–7.85 (m, 6 H), 3.20–3.75 (m, 3 H), and 1.52–3.17 (m, 2 H); IR ($CHCl_3$) 3340, 3325, 1710, and 1045 cm^{-1}.

Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 57.40; H, 5.30; N, 6.69. Found: C, 57.42; H, 5.38; N, 6.72.

2-Ethoxy-3-phenylthio-1,2-dehydropyrrolidine (6). A 1:2:1 Ratio with HMPA. Following the general procedure A, the imidate anion (0.0354 mol) was prepared in the presence of LDA (0.0708 mol) in the usual way in 30 mL of dry THF. The reaction mixture was stirred at −78 °C for 35 min. Phenyl disulfide (7.72 g, 0.0354 mol) dissolved in 15 mL of THF containing HMPA (6.34 g, 0.0354 mol) was added over a 7-min period. The addition funnel was rinsed with 5 mL of THF, and the resulting reaction mixture was stirred at −78 °C for 35 min. The reaction mixture was allowed to warm to −20 °C, stirred at −20 °C for 20 min, and then allowed to warm to room temperature. Workup as usual yielded an oil. The oil was distilled twice to afford 3.6 g (46%) of **6**: bp 95–100 °C (0.05 mm); NMR (CCl_4) δ 7.05–7.58 (m, 5 H), 4.13 (q), and 3.73–3.96 (m, 3 H), 3.39 (t, 2 H), 1.62–2.76 (m, 2 H) and 1.27 (t, 3 H).

Anal. Calcd for $C_{12}H_{15}NOS$: C, 65.12; H, 6.83; N, 6.32. Found: C, 65.08; H, 6.74; N, 6.20.

1-Methyl-3-phenylthio-2-pyrrolidinone (9) and 1-Methyl-3,3-diphenylthio-2-pyrrolidinone (11). A 1:2:1 Ratio. Following the general procedure A, the enolate of *N*-methyl-2-pyrrolidinone (0.0404 mol) was prepared in the presence of LDA (0.0808 mol) in the usual manner in 30 mL of THF. The reaction mixture was stirred at −78 °C for 35 min. Phenyl disulfide (8.81 g, 0.0404 mol) dissolved in 20 mL of THF was added dropwise over a 10-min period. The reaction mixture was stirred at −78 °C for 35 min. The reaction mixture was allowed to warm to −20 °C, stirred at −20 °C for 20 min, and then allowed to warm to room temperature.

Workup as usual yielded an oil. The oil was chromatographed on silica gel G, and elution with ether–hexane solutions and ether afforded 4.5 g (54%) of **9** and 141 mg (2%) of **11**. The NMR and TLC analyses of compounds **9** and **11** were consistent when compared with those of authentic[2] **9** and **11**.

1-Methyl-3-phenylthio-2-piperidone (10). A 1:2:1 Ratio. Following the general procedure A, the enolate of 1-methyl-2-piperidone (0.0354 mol) was prepared in the presence of LDA (0.0707 mol) in the usual way in 35 mL of THF. The reaction mixture was stirred at −78 °C for 35 min. Phenyl disulfide (7.72 g, 0.0354 mol) dissolved in 20 mL of THF was added over a 15-min period. The reaction mixture was stirred at −78 °C for 35 min. The reaction mixture was allowed to warm to −20 °C, stirred at −20 °C for 20 min, and then allowed to warm to room temperature.

Workup as usual yielded an oil. The oil was chromatographed on silica gel G and elution with ether–hexane and ether solutions afforded 6.0 g (77%) of **10**, bp 155 °C (0.05 mm). The NMR and TLC analyses of compound **10** were consistent when compared with those of authentic[2] **10**.

1-Methyl-3-phenylthio-2-pyrrolidinone (9) and 1-Methyl-3,3-diphenylthio-2-pyrrolidinone (11). A 1:2:2 Ratio. Following the general procedure A, the enolate of 1-methyl-2-pyrrolidinone (0.040 mol) was prepared in the presence of LDA (0.080 mol) in the usual manner in 35 mL of THF. The reaction mixture was stirred at −78 °C for 35 min. Phenyl disulfide (17.6 g, 0.080 mol) dissolved in 35 mL of THF was added dropwise over a 15-min period. The reaction mixture was stirred at −78 °C for 35 min. The reaction mixture was allowed to warm to −20 °C, stirred at −20 °C for 20 min, and then allowed to warm to room temperature.

Workup as usual yielded a white solid. The solid was triturated with a 50% ether–hexane solution to afford 9.2 g (72%) of **11**, mp 87–88.5 °C. The mother liquor was chromatographed on silica gel G, and elution with ether and methanol–ether solutions afforded an additional 1.4 g (11%) of **11** and 460 mg (6%) of **9**. Total yield of **11** was 83%. The NMR and TLC analyses of compounds **9** and **11** were consistent when compared with those of authentic[2] **9** and **11**.

1-Methyl-3,3-diphenylthio-2-piperidone (12). A 1:2:2 Ratio. Following the general procedure A, the enolate of 1-methyl-2-piperidone (0.0354 mol) was prepared in the presence of LDA (0.0707 mol) in the usual way in 50 mL of dry THF. The reaction mixture was stirred at −78 °C for 35 min. Phenyl disulfide (15.41 g, 0.0707 mol) dissolved in 35 mL of THF was added over a 15-min period. The reaction mixture was stirred at −78 °C for 35 min. The reaction mixture was allowed to warm to −20 °C, stirred at −20 °C for 20 min, and then

allowed to warm to room temperature. Workup as usual yielded a white solid. Trituration of the solid with a 50% ether–hexane solution afforded 6.5 g (56%) of **12**, mp 136–137 °C. The mother liquor was chromatographed on silica gel G, and elution with ether–hexane solutions and ether afforded an additional 675 mg (6%) of **12** and 1.2 g (15%) of **10**. Total yield of **12** was 62%. The NMR and TLC analyses of compounds **10** and **12** were consistent when compared with those of authentic[2] **10** and **12**.

1-Methyl-3,3-diphenylthio-2-piperidone (12). Inverse Quenching. A 1:2:2 Ratio. Following the general procedure B, the amide enolate (0.00885 mol) was prepared in the usual way in 13 mL of THF in the presence of LDA (0.0177 mol). The reaction was stirred at −78 °C for 10 min. The enolate solution was siphoned through a glass tube into a solution of phenyl disulfide (3.85 g, 0.0177 mol) dissolved in 10 mL of THF at 0 °C. The resulting reaction mixture was stirred at 0 °C for 1.5 h. Workup as usual yielded a solid. The solid was triturated with a 50% ether–hexane solution to afford 2.2 g (76%) of **12**, mp 136–37.5 °C. The NMR and TLC analyses of compound **12** were consistent when compared with those of authentic[2] **12**.

1-Methyl-3-phenylsulfinyl-2-pyrrolidinone (13). Following the general procedure A, LDA (0.0202 mol) was prepared in the usual manner in 10 mL of THF. The reaction mixture was cooled to −78 °C and 1-methyl-2-pyrrolidinone (1 g, 0.0101 mol) dissolved in 20 mL of THF was added over a 15-min period. The reaction mixture was allowed to stir at −78 °C for 1 h. Methyl benzenesulfinate (1.57 g, 0.0101 mol) dissolved in 5 mL of THF was added over a 5-min period. The reaction was stirred at −78 °C for 1 h, then allowed to come to room temperature, and stirred overnight. The reaction mixture was poured into a 10% hydrochloric acid solution and extracted with two 200-mL portions of $CHCl_3$. The chloroform extracts were combined, washed with a saturated NaCl solution, dried over anhydrous $MgSO_4$, filtered, and concentrated on a rotary evaporator, affording a yellow oil. The oil was chromatographed on silica gel G, and elution with ether–hexane solutions, ether, and ether–chloroform solutions afforded 2.2 g (96%) of pure **13** as a white solid: the NMR and TLC analyses of **13** were consistent when compared with those of authentic **13**.[3]

Registry No.—**1**, 14468-90-7; **2**, 65102-72-9; **3**, 65102-73-0; **4**, 65102-74-1; **5**, 931-46-4; **6**, 65138-32-1; **7**, 872-50-4; **8**, 931-20-4; **9**, 59953-50-3; **10**, 59953-51-4; **11**, 59953-53-6; **12**, 59953-54-7; **13**, 63914-40-9; **14**, 65102-75-2; phenyl disulfide, 882-33-7; methyl benzenesulfinate, 670-98-4.

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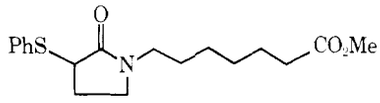

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Clarification of the Mechanism of the Reaction of Terminal Propargylic Chlorides with Alkyl Grignard Reagents

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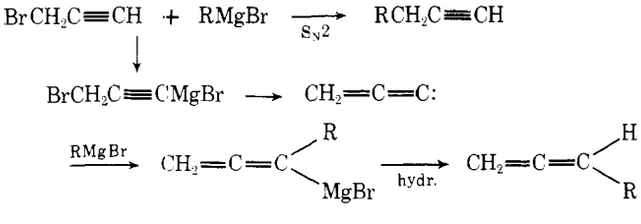
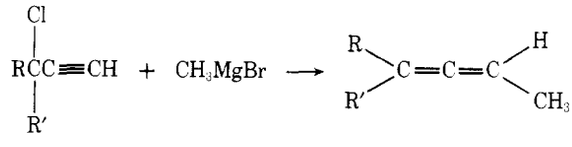
In the absence of transition metal impurities in the magnesium used to prepare the alkyl Grignard reagent, terminal propargylic chlorides react with Grignard reagents to form an allene carbene–zwitterion intermediate. Reaction of this intermediate with a second molecule of the Grignard reagent generates a mixture of propargyl and allenyl Grignard reagents which on hydrolysis generates a mixture of two alkynes and the allene. No evidence was found for the occurrence of carbonium ion, free radical, or S_N2' reaction pathways.

The history of the reaction of propargyl derivatives with Grignard reagents is one of confusion, widely divergent results being reported by various authors. Serratosa[1] has suggested that propargyl bromide can react with Grignard reagents via two mechanistic pathways, one being a direct S_N2 process to



produce exclusively alkyne, and the other occurring via an allene–carbene to give exclusively allene. Pasternak and Delépine[2] have reported that terminal tertiary propargylic halides react with methylmagnesium bromide to produce only allene in quantitative yields! (No mechanism was proposed.) These authors also suggested that the previous contradictory reports of the formation of mixtures of isomeric allenes, alkynes, and dienes were due to isomerization during the hydrolysis step.



Coulomb-Delbecq[3] and co-workers have investigated the reactions of propargylic acetates with Grignard reagents in the absence and presence of added magnesium iodide or cobalt chloride. In the presence of added magnesium iodide a mixture of products is obtained in which allene and alkyne are formed in greater amounts than in the absence of magnesium iodide, leading the authors to propose that a propargyl–allenyl cation was an intermediate. However, in the presence of cobalt chloride substantially higher yields of allene were formed, leading the authors to suggest that an intermediate propargyl–allenyl radical was involved as an intermediate. Substantial yields of dimeric products were also reported in both cases.

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