hydride (132 mg, 5.5 mmol) in tetrahydrofuran (8 mL) was stirred at room temperature for 2 h. Methyl iodide (0.44 mL, 1.00 g, 7.1 mmol) was added and the solution refluxed for 2 h. After cooling, ether (30 mL) was added and the solution was washed with 1 N sodium hydroxide (3 × 10 mL) and water (3 × 10 mL) and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was separated by preparative thick layer chromatography on silica gel using ether/methylene chloride (1:9) as eluent to give **8a** (0.87 g, 68%, mp 63–64 °C): IR (neat) 5.74, 5.88, 6.18 μm; ^{1}H NMR δ 1.20 (3 H, triplet, J = 7.5 Hz), 1.55 (3 H, singlet), 2.96 (3 H, singlet), 4.17 (2 H, quartet, J = 7.5 Hz), 6.70–6.88 (2 H, 3 singlets), 7.36–7.70 (2 H, multiplet).

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. DA 01552-2).

Registry No.—**5a,** 67271-23-2; **5b,** 67271-24-3; **5c,** 67271-25-4; **6a,** 61838-88-8; **6b,** 67271-26-5; **6c,** 67271-27-6; **8a,** 67271-28-7; **10a,** 67271-29-8; **10b,** 67271-30-1; **10c,** 67271-31-2; *N*-methylaniline, 100-61-8; ethyl 2-bromoacetoacetate, 609-13-2; ethyl 2-chlorobutyroylacetate, 67271-32-3; ethyl 2-chlorobenzoylacetate, 41381-97-9; 1-methyloxindole, 61-70-1; ethyl chloroformate, 541-41-3; ethyl 1-methyloxindole-3-carboxylate, 39478-72-3; ethyl 1-methylindoxyl-2-carboxylate, 67271-33-4.

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Condensation Reactions of Carbanions and Ylides Derived from α-Halo Sulfoximines

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The homologation of aldehydes and ketones is a classic problem in organic chemistry with many practical solutions. The limitations and disadvantages of the known methods are sufficient to warrant development of new methods. We have recently described the first preparations of α-halo sulfoximines[1] and we envisioned in their chemistry a carbonyl homologation scheme (Scheme I).

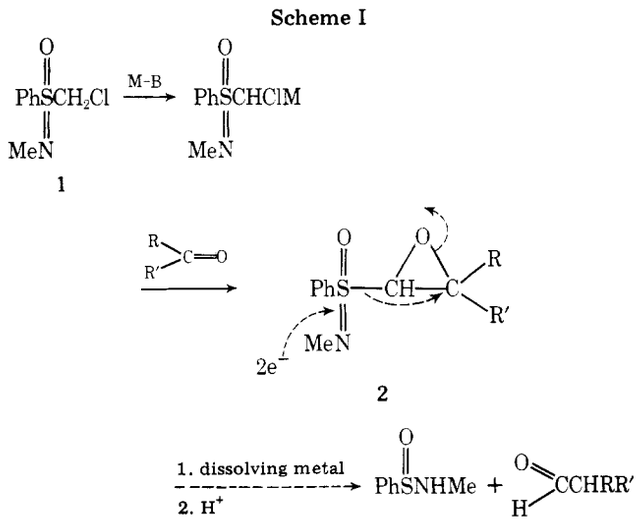
After considerable experimentation, the most effective condition which we found for the condensation of **1** with carbonyl compounds involved potassium *tert*-butoxide in a mixture of dimethyl sulfoxide (Me_2SO) and tetrahydrofuran (THF) at 0 °C to room temperature. Table I lists the epoxy sulfoximines produced in this manner. The use of symmetrical ketones simplified product analysis by restricting the diastereomers to two in each case. Chromatography on basic alumina was found to be acceptable for the isolation of the epoxy sulfoximines. Attempts to condense **1** with *p*-nitrobenzaldehyde and 2-propenal under the above conditions were unsuccessful. The diastereomeric alcohols **3** and **4** were obtained in good yield by using sodium hydride in THF at 0 °C. All four diastereomeric α-chloro-β-hydroxy sulfoximines (**3**) were separated and characterized by NMR spectroscopy. All attempts to effect ring closure of **3** and **4** to epoxy sulfoximines have been unsuccessful.

Table I. Condensation of 1 with Carbonyl Compounds

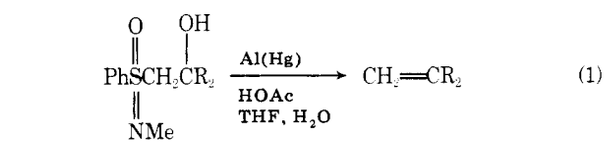
carbonyl compound	registry no.	product	R	R′	yield, %	diastereomeric ratio[a]
acetone	67-64-1	**2a**	CH_3	CH_3	81	29/72
cyclohexanone	108-94-1	**2b**	$-(CH_2)_5-$		75	32/68
4-*tert*-butylcyclohexane	98-53-3	**2c**	$-(CH_2)_2-CH(t\text{-Bu})-(CH_2)_2-$		50	*b*
benzaldehyde	100-52-7	**2d**	H	Ph	75	44/56

[a] Diastereomers due to contiguous chiral centers at S and the α-C. [b] Mixture of four diastereomers due to chiral centers at S and the α-C plus cis–trans ring isomers. The diastereomers with the *tert*-butyl and oxide cis accounted for 90% of the product.

Scheme I



Aluminum amalgam in the presence of acetic acid in aqueous THF has been found effective for the reductive elimination of β-hydroxy sulfoximines to yield alkenes (eq 1).[2]



(1)

When the epoxy sulfoximines **2a** and **2b** were treated under the above conditions no isobutyraldehyde or cyclohexanecarboxaldehyde could be detected by gas chromatography. Thin-layer chromatography indicated rapid loss of the starting material. From the reaction of **2b,** cyclohexylmethanol was isolated. In the absence of acetic acid **2b** is slowly reduced to **5** (eq 2). Although the above experiments are not exhaustive we have concluded that Scheme I is not likely to provide a practical method for homologation of aldehydes and ketones.

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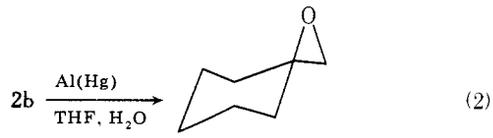
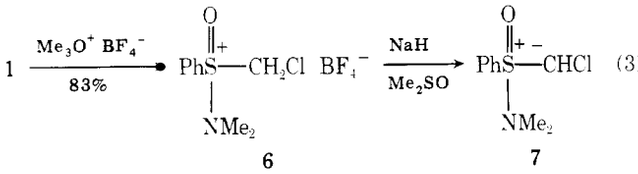


(2)

Epoxy sulfoximines may be interesting substrates for other types of reactions.

The use of sulfoximine derivatives as nucleophilic alkylidene transfer reagents has been described earlier.[3] To test the feasibility of chloromethylene transfer to Michael acceptors the reactions shown in eq 3–5 were examined.



(3)

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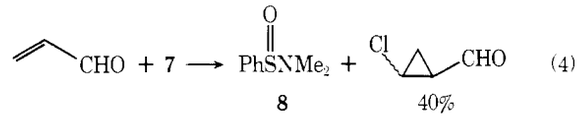

(4)

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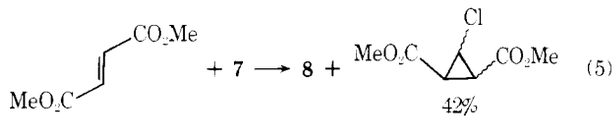

(5)

In the examples shown, the corresponding chlorocyclopropane derivatives were obtained in moderate yields. The isomeric 2-chlorocyclopropyl-1-carboxaldehydes (**9**) were isolated as dinitrophenylhydrazones.

Experimental Section

2,2-Dimethyl-3-(*N*-methylphenylsulfonimidoyl)oxirane (2a). Under a dry nitrogen atmosphere, a solution of 1.06 g (5.2 mmol) of *S*-(chloromethyl)-*N*-methyl-*S*-phenylsulfoximine in 15 mL of THF–Me_2SO (1:2 by volume) was cooled in an ice bath. Addition of 0.66 g (5.9 mmol) of potassium *tert*-butoxide (MSA Research Corp.) produced a red solution. With continuous stirring 1.15 mL (3 equiv) of acetone was added via syringe. The solution was stirred at 0 °C for 3 h and at room temperature for an additional 4 h. The reaction mixture was poured into an equal volume of saturated ammonium chloride and extracted three times with equal volumes of ether. The ether extracts were washed with several portions of water, dried (Na_2SO_4), and concentrated by rotary evaporation to give 0.95 g (81%) of crude oil. The NMR spectrum of this oil indicated a 28:72 mixture of diastereomeric epoxy sulfoximines. Chromatography (silica gel/ether) and fractional crystallization (ether–pentane) resulted in 0.3 g of one diastereomer as a white crystalline solid, mp 79.5–80.5 °C.

2-(*N*-Methylphenylsulfonimidoyl)-1-oxaspiro[2.5]octane (2b). Under a nitrogen atmosphere, 4.06 g (19.6 mmol) of *S*-(chloromethyl)-*N*-methyl-*S*-phenylsulfoximine was dissolved in a mixture of 5 mL of THF (distilled from Na) and 17 mL of Me_2SO (distilled from CaH_2). The solution was cooled in an ice bath. Addition of 2.26 g (20.0 mmol) of potassium *tert*-butoxide resulted in a red-brown solution. After the addition of 4.1 mL (2 equiv) of freshly distilled cyclohexanone the reaction mixture was treated as described for **2a** to give 4 g (75%) of crude brown oil. The NMR spectrum of this oil showed the presence of both diastereomeric epoxy sulfoximines. Approximately 1 g of the oil was dissolved in ether (5 mL) and cooled to −78 °C. Scratching induced crystallization. Recrystallization (pentane–ether) resulted in the isolation of one diastereomer as a white crystalline solid, mp 95–95.5 °C.

6-*tert*-Butyl-2-(*N*-methylphenylsulfonimidoyl)-1-oxaspiro[2.5]octane (2c). Under a nitrogen atmosphere 4.02 g (17.4 mmol) of *S*-(chloromethyl)-*N*-methyl-*S*-phenylsulfoximine was dissolved in a mixture of 7 mL of THF (distilled from Na) and 15 mL of Me_2SO (distilled from CaH_2). The solution was cooled in an ice bath. Addition of 2.36 g (21.0 mmol) of potassium *tert*-butoxide resulted in a red-brown solution. With continuous stirring 6.11 g (40.0 mmol) of 4-*tert*-butylcyclohexanone dissolved in 3 mL of THF and 5 mL of Me_2SO was added via syringe. After stirring 2 h at 0 °C the ice bath was removed and stirring was continued 16 h. The workup followed that described for **2a**. The crude oil was subjected to fractional sublimation and steam distillation to remove unreacted ketone to give 2.79 g of a red-brown oil which was finally subjected to column chromatography. A total of 2.0 g of impure epoxy sulfoximine was obtained. The NMR indicated the presence of diastereomers.

***trans*-1-(*N*-Methylphenylsulfonimidoyl)-2-phenyloxirane (2d).** Under a nitrogen atmosphere 1.4 g (7 mmol) of *S*-(chloromethyl)-*N*-methyl-*S*-phenylsulfoximine was dissolved in 3.0 mL of THF (distilled from Na) and 8.0 mL of Me_2SO (distilled from CaH_2). The solution was cooled to 0 °C in an ice bath. Addition of 0.79 g (7 mmol) of potassium *tert*-butoxide resulted in a red-brown solution. With continuous stirring 1.72 mL (2 equiv) of benzaldehyde was added. After stirring for 30 min at 0 °C the ice bath was removed and stirring was continued for 3 h. Workup as for **2a** gave a crude oil. The oil was dissolved in carbon tetrachloride (50 mL) and concentrated again to give 0.907 g (75%) of oil. Column chromatography (silica gel/ether) gave 0.24 g of a mixture (44:56) of diastereomeric epoxy sulfoximines. Pure *N*-methylbenzenesulfinamide was also isolated from the chromatography and identified by IR and NMR.

2-Chloro-2-(*N*-methylphenylsulfonimidoyl)-1-(4-nitrophenyl)ethanol (3). To a cold (−78 °C) solution of 1.63 g (8.0 mmol) of *S*-(chloromethyl)-*N*-methyl-*S*-phenylsulfoximine in 8 mL of dry THF was added 3.90 mL (8.0 mmol) of 2.05 M butyllithium. A yellow solution resulted. Addition of 1.69 g (12.0 mmol) of 4-nitrobenzaldehyde in 5 mL of THF was made in one portion. After stirring for 45 min the dark red solution was poured into an equal volume of saturated ammonium chloride and extracted twice with 100-mL portions of ether. The extracts were washed with 10% aqueous sodium hydrogen sulfite and then water. Drying over sodium sulfate and concentrating by rotary evaporation gave 2.26 g of a crude yellow solid. This material was found to be a mixture of four diastereomers. By a combination of fractional crystallization and thick-layer chromatography each of the four diastereomers was isolated in high enough purity that the proton resonance for each could be measured. Spectal data for diastereomers A, B, C, and D have been included in the microfilm edition.

1-Chloro-1-(*N*-methylphenylsulfonimidoyl)-3-buten-2-ol (4). A solution of 0.622 g (3.06 mmol) of *S*-(chloromethyl)-*N*-methyl-*S*-phenylsulfoximine in 10.0 mL of THF (distilled from Na) was cooled to −78 °C and 1.51 mL of 2.05 M *n*-butyllithium was added. A pale yellow solution was obtained. After stirring 5 min at −78 °C 0.21 mL (3.1 mmol) of 2-propenal (freshly distilled) was added in one portion. The reaction flask was stoppered, wrapped with Parafilm, and placed in the freezer (−38 °C) for 11.5 h. The yellow solution was poured into an equal volume of saturated ammonium chloride and extracted with two equal volumes of ether. The extracts were washed with 10% aqueous sodium hydrogen sulfite and water. Drying (Na_2SO_4) and concentrating resulted in 0.726 g of slightly yellow oil. The α-chloro-β-hydroxy sulfoximine was further purified by thick-layer chromatography to give 0.29 g of **4** (36%).

Reduction of 2c with Aluminum Amalgam in Aqueous THF. A total of 0.53 g (~1.6 mmol) of the diastereomeric epoxy sulfoximine (**2c**) contaminated with ~10–20% 4-*tert*-butylcyclohexanone was dissolved in 30 mL of 10% aqueous THF. After adding 0.94 g (16.0 g-atom) of aluminum amalgam, the mixture was stirred at room temperature for 48 h and then filtered. Addition of 20 mL of water was followed by extraction with ether. The extracts were dried (Na_2SO_4) and concentrated via rotary evaporation to give 0.28 g of pale yellow oil. Column chromatography (basic Al_2O_3/ether) gave 0.107 g of a mixture of isomeric 6-*tert*-butyl-1-oxaspiro[2.5]octanes. The ratio of cis (*tert*-butyl and oxide) to trans isomers was found to be 90:10 by NMR (by comparison of the NMR spectrum to those of authentic samples).

(Chloromethyl)[(dimethylamino)phenyl]oxosulfonium Fluoroborate (6). To 1.020 g (5.02 mmol) of *S*-(chloromethyl)-*N*-methyl-*S*-phenylsulfoximine in 25 mL of dichloromethane was added in one portion 0.773 g (5.23 mmol) of trimethyloxonium fluoroborate. A heterogenous mixture was obtained that became homogeneous after 15 min. After stirring for 30 min diethyl ether was added to precipitate the fluoroborate salt (1.264 g, 82.9%). Recrystallization from methanol gave fine white needles, mp 159.5–160.5 °C.

Reaction of (Dimethylamino)phenyloxosulfonium Chloromethylide with Dimethyl Fumarate. In a flamed out flask purged with dry nitrogen was added 0.056 g (1.3 mmol) of sodium hydride (57% oil dispersion). The oil was removed by washing with pentane. The last traces of pentane were blown off in a stream of nitrogen. The sodium hydride was slurried in 1.0 mL of THF (distilled from Na) and 2.0 mL of Me_2SO (distilled from CaH_2) and cooled in an ice bath. A total of 0.4 g (1.3 mmol) of **6** in 2.0 mL of Me_2SO was added dropwise. After 5 min hydrogen ceased evolving and a yellow solution was obtained. While stirring at 0 °C, 0.189 g (1.3 mmol) of dimethyl fumarate

in 1.8 mL of THF was added in one portion. The ice bath was removed and the solution was stirred at room temperature for 12 h. The brown solution was poured into an equal volume of cold aqueous ammonium chloride and extracted with two equal volumes of ether. The extracts were backwashed with water, dried ($MgSO_4$), and concentrated by rotary evaporation to give 0.36 g of a brown semisolid. Column chromatography (silica gel/30% ether–cyclohexane) resulted in 0.11 g (42%) of a diastereomeric mixture of 1,2-bis(carbomethoxy)-3-chlorocyclopropane and 0.13 g (60%) of *N,N*-dimethylbenzenesulfinamide.

Reaction of 7 with 2-Propenal. The reaction was carried out in the manner described above. The extraction was done with pentane. Some product codistilled with pentane, but the residue after concentration and treatment with 2,4-dinitrophenylhydrazine yielded 40% of 2-chlorocyclopropanecarboxaldehyde as its 2,4-dinitrophenylhydrazone, mp 160–161 °C. In a separate run, *N,N*-dimethylbenzenesulfinamide was found to be produced in 81% yield.

Acknowledgment. This research was supported by the National Science Foundation.

Registry No.—**1**, 67069-79-8; **2a** isomer 1, 67069-67-4; **2a** isomer 2, 67069-68-5; **2b** isomer 1, 67069-69-6; **2b** isomer 2, 67069-70-9; **2c**, 67069-71-0; **2d** isomer, 67112-77-0; **2d** isomer 2, 67069-63-0; **3** isomer 1, 67112-78-1; **3** isomer 2, 67112-76-9; **3** isomer 3, 67069-62-9; **3** isomer 4, 67145-49-7; **4**, 67069-72-1; **6**, 67069-74-3; **7**, 67069-75-4; **8**, 5539-54-8; **9** isomer 1, 67069-76-5; **9** isomer 2, 67069-77-6; *cis*-6-*tert*-butyl-1-oxaspiro[2.5]octane, 7787-78-2; *trans*-6-*tert*-butyl-1-oxaspira[2.5]-octane, 18881-26-0; 1,2-bis(carbomethoxy)-3-chlorocyclopropane, 67069-78-7; 4-nitrobenzaldehyde, 555-16-8; 2-propenal, 107-02-8; dimethyl fumarate, 624-49-7.

Supplementary Material Available: Analytical and spectral data of the compounds discussed in this paper (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) C. R. Johnson and H. G. Corkins, *J. Org. Chem.*, companion paper in this issue.
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(3) C. R. Johnson, *Acc. Chem. Res.*, **6**, 341 (1973).

Temperature-Dependent Rearrangement of 2-(2-Furyl)-2-lithio-1,3-dithiane

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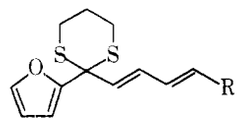
In the course of our work directed in the area of the Diels–Alder reaction, we required the preparation of compounds such as **1**. It was thought the use of 2-(2-furyl)-1,3-dithiane



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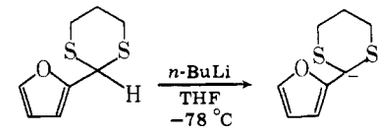
(**2**) as a nucleophilic acylating agent would provide an efficient entry into such a system. The use of lithiated 1,3-dithianes is well known and is the subject of two excellent reviews by Seebach.[1,2] Interestingly, the synthesis and use of compound **2** had not previously been recorded in the literature. We wish to report the preparation of **2** and the temperature dependent rearrangement of the anion produced from **2**.

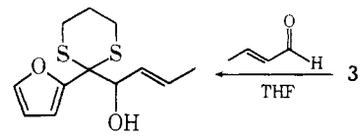
Results and Discussion

Preparation and Metalation of 2-(2-Furyl)-1,3-dithiane. The preparation of dithiane **2** was accomplished in



2 3

75% yield from furfural using the method of Corey and Seebach.[3] Metalation of **2** is complete within 10 min at −78 °C (method A). Reaction of anion **3** at −78 °C with crotonaldehyde and ethyl formate led to the isolation of alcohol **4** and aldehyde **5** in 95 and 60% yields, respectively.



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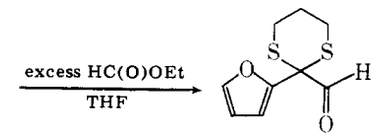

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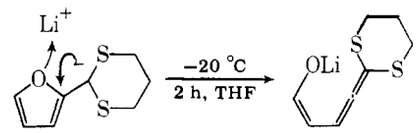
Temperature-Dependent Rearrangement of 3. When metalation was attempted using the method of Corey and Seebach[3] (method B), anion **3** underwent a novel rearrangement resulting in the formation of **6**. Analogy for such a re-



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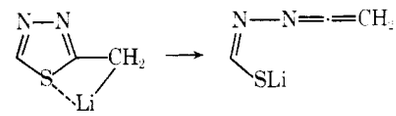
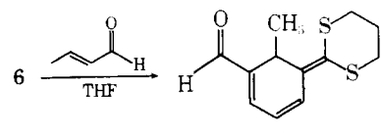
arrangement has previously been reported in the literature.[4] The rearrangement of 2-lithiomethylthiadiazoles reported by Meyers was also shown to be temperature dependent.[4a]



Compound **6** is postulated to account for the unexpected formation of ketene thioacetal **7**, the result of quenching the anion produced by method B with crotonaldehyde at −78 °C. Structural assignment **7** is based on the spectral characterization data (Experimental Section). The formation of **7** could be envisioned by one of two possible mechanisms. Compound **7** could arise from a 1,4 addition to crotonaldehyde at the γ



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position of dienolate **6**, followed by cyclization and subsequent loss of H_2O. The other possibility is a Diels–Alder addition of **6** with crotonaldehyde followed by elimination of water after acidification.[5]

Further insight into the rearrangement was gained by quenching **6** with trimethylchlorosilane. Aqueous workup of the reaction furnished the cis unsaturated aldehyde **9** in quantitative yield. The structure is based on spectral data and the conversion of **9** to *n*-pentyl alcohol by successive treatment with $NaBH_4$ and Raney-Nickel.[6] The coupling constant of 7.5 Hz between H_2 and H_3 is indicative of a cis double bond when compared to *trans*-2-penten-4-ynal, a known trans-α,β-un-

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