diazotiert und bei 100° mit *p*-Kresol umgesetzt. Die Aufarbeitung durch Acetylierung, fraktionierte Destillation (Siedegrenzen 140–165°/0,3 Torr), Chromatographie und Verseifung liefert nach mehrfachem Umkristallisieren aus Äthanol 0,3 g reines *5,5'-Dimethyl-2'-(1-piperidyl)-2-biphenylol* vom Smp. 167–169°, das in allen physikalischen Eigenschaften mit dem durch thermische Umlagerung von **2** erhaltenen **3** identisch ist.

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72. [2,3] Sigmatropic Rearrangements on Lithiation of Some Allyl Sulfides

Preliminary Communication 1)

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(5 II 71)

Summary. In five cases, [2,3] sigmatropic rearrangement of the type

has been observed.

Baldwin [1] and *Ollis* [2] and their coworkers have recently proposed a model for the enzymatic coupling of two farnesyl units to yield squalene. The two units are first linked by a disulfide bridge. The disulfide, *via* [2,3] sigmatropic change, is in equilibrium with a small amount of a farnesyl nerolidyl disulfide [3], from which, by desulfurisation [4], farnesyl nerolidyl sulfide is formed. The carbon carbon bond between the sulfur bridged units is then created intramolecularly by a second [2,3] sigmatropic rearrangement of a derived sulfonium ylid [1] [2].

Baldwin et al. [1], in their model, have generated the ylid by alkylation of the sulfide and reaction of the resulting sulfonium salt with n-butyllithium. However, under the conditions of the alkylation, the sulfide tends to isomerise to the symmetrical isomer [1] [2]. *Ollis et al.* [2] circumvented this difficulty by bringing the farnesyl nerolidyl sulfide into reaction with benzyne, which leads to the ylid directly, by addition to sulfur and deprotonation next to it.

Protons can be readily removed from allyl [5] and benzyl [5c] [6] sulfides and an allylic [5b] and a *Sommelet* rearrangement [6] have been observed in the resulting carbanionoid species. This suggests that on direct metallation of the farnesyl nerolidyl

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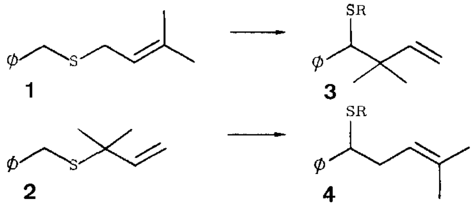
1) Full paper to appear in Helv.

sulfide (or analogue with different substituents), [2,3] sigmatropic change2) with formation of a metal thiolate might occur. This new rearrangement would be analogous to that of the corresponding ylids, and more directly, to the *Wittig* rearrangement of allyl ethers [7] [8] [9]. It might constitute an interesting synthetic variant of the *Baldwin-Ollis* scheme.

In connection with our work on the *Wittig* rearrangement [7], we have studied this reaction and found it a very efficient method for the synthesis of thiols, methyl sulfides and hydrocarbons of the squalene type or with the artemisyl skeleton. The recent report by *Biellmann & Ducep* [10] on this subject prompts us to report our results.

Reaction of sulfides **1** and **2** with 1.4 equiv. of butyllithium3) in tetrahydrofuran solution at – 30° for 1.5 and 5 h and subsequent treatment of the products with 2 equiv. of methyl iodide for 2 min, gave methyl sulphides **3** (R = CH_3) and **4** (R = CH_3), respectively, in almost quantitative yields.



On gas chromatographic analysis, **4** (R = CH_3) could not be detected in the product obtained from **1**, and, conversely, **3** (R = CH_3) could not be detected in the product from **2** ($< 0.3 - 0.5\%$). Even when **1** was treated with butyllithium in tetrahydrofuran at + 45° and the product then methylated at – 30°, **4** (R = CH_3) could not be detected ($< 0.3 - 0.5\%$).

Reaction of sulfides **1** and **2** as described and subsequent hydrolysis of the products, led to thiols **3** (R = H) and **4** (R = H), respectively, in almost quantitative yields.

Reaction of **1** as described, followed after 4 min by addition of excess deuterium oxide and working up in water, gave a ca. 2:1 mixture of **1** and **3** (R = H). According to n.m.r. and mass spectrometry, deuterium had not been incorporated4) into recovered **1**.

We interpret these results as follows. **1** and **2** are lithiated in the benzyl position. The lithium compounds so formed rearrange rapidly by [2,3] sigmatropic change2). The reaction with butyllithium is the rate-determining step. Competitive rearrangement via dissociation-recombination2) (which would give **3** and **4** from either **1** or **2**) is not detected.

Reaction of sulfides **5** and **6** with butyllithium in tetrahydrofuran at – 30° for 4 h, followed by hydrolysis or methylation of the products, gave **7** (R = H or CH_3)

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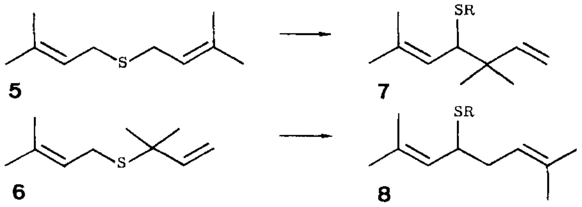
2) [2,3] Sigmatropic and dissociation-recombination pathways in such a rearrangement have been discussed in detail for the oxygen analogue, the *Wittig* rearrangement [7] [8] [9].

3) Commercial n-butyllithium in hexane, diluted to ca. 1.7 N, was used.

4) Similar treatment of t-butyl benzyl sulfide (– 30°, 2 h) and of methyl benzyl sulfide, led to incorporation of close to one deuterium in the benzyl positions.

and **8** (R = H or CH_3), respectively, in almost quantitative yields. Again, only the products of [2,3] sigmatropic change are detected.

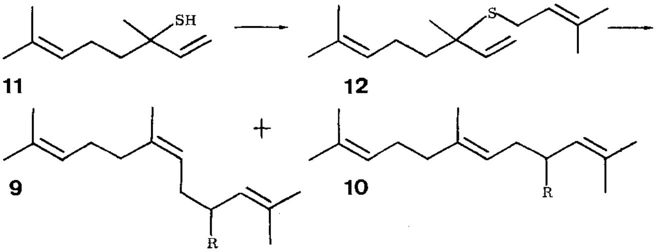


5 **7**

6 **8**

In the analogous rearrangements of allyl sulfonium ylids [11] and of lithiated allyl ethers [7] [8] [9], rearrangement by a dissociation-recombination mechanism competes with the [2,3] sigmatropic pathway. Its absence[5] in the cases described here probably reflects the instability of the thioaldehyde anion radical fragments which would have to be formed in such a process. This situation might change if different substituents were introduced[6].

The synthetic potential of the reaction is further demonstrated by the synthesis of the sesquiterpenoid, squalene-like, *cis-trans* isomeric hydrocarbons **9** (R = H) and **10** (R = H). Thiolinalool **11** was converted into sulfide **12** by treatment with butyllithium (tetrahydrofuran, 1 equiv, – 70°, 5 min), followed by alkylation of the lithium thiolate formed with 1-chloro-3-methylbut-2-ene (tetrahydrofuran, 2 equiv., – 30°, 14 h) in 84% yield. Reaction of **12** with butyllithium (tetrahydrofuran, 1.5 equiv., – 30°, 5 h) and alkylation of the product with methyl iodide (2 equiv., – 30°, 5 min) gave a ca. 2:3 mixture of methyl sulfides **9** (R = SCH_3) and **10** (R = SCH_3) in 84% yield. Reduction of this mixture with excess lithium in ammonia-tetrahydrofuran led to the mixture of hydrocarbons **9** (R = H) and **10** (R = H) in 87% yield.



11 **12**

9 **10**

As starting materials for this reaction, sulfides of types **5** and **6** are readily available. Tertiary thiols of type **11** as precursors of unsymmetrical sulfides of type **12** can

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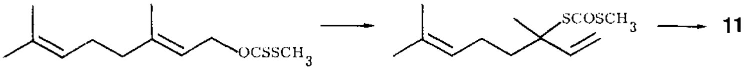
[5] *Hauser* reports [6], that dibenzyl sulfide, on metallation undergoes *Sommelet* rearrangement, that is, a [2,3] sigmatropic change involving the benzene ring (however, see ref. [12]). We find that lithiated t-butyl benzyl sulfide[4] is stable at room temperature under our conditions; a slow cleavage with formation of lithium benzylthiolate occurs, presumably by α',β-elimination [13]. In contrast, both dibenzyl ether and benzyl t-butyl ether readily undergo *Wittig* rearrangement [9].

[6] This could be the case in the reaction decribed in ref. [5f].

be prepared by dithiocarbonate rearrangement[7]). Thus, **11** was obtained as follows. Geraniol was converted into O-geranyl S-methyl dithiocarbonate by successive treatment with butyllithium, carbon disulfide and methyl iodide. On distillation it rearranged to S-linalyl S-methyl dithiocarbonate (86%, based on geraniol), which was cleaved[8]) with lithium aluminium hydride [15] to give **11** (75%). 2-Methylbut-3-en-2-thiol, from which **2** was made, was obtained by an analogous sequence.



Further work on the reactions reported here, and on the chemistry of the various allyl thiols obtained, is in progress.

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[8]) Treatment with aqueous potassium hydroxide gave thiogeraniol.

[7]) This reaction is known in several variants [14].