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Generation and Rearrangement of C_2-Symmetric Chiral Allyl Anions derived from Dibenzo- and 1,1'-Dinaphtho-2,2'-dithiopropenes[1]

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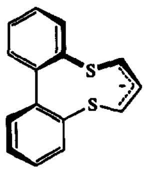
Key Words: 1,3-Dithioallyl anions, dibenzo-2,2'-dithiol, 1,1'-dinaphtho-2,2'-dithiol, atropisomeric sulfur reagents, C_2-symmetric chiral reagents.

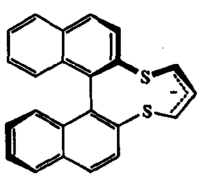
Abstract: The allyl anions generated from 4*H*-dinaphtho[2,1-*f*:1',2'-*h*][1,5]dithionin (**6**) and 2-ethenyl-dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepin (**8**) rearranged both to the thiolate **10** which further reacted with water or methyl iodide to afford **9** or **12** respectively. A similar behavior was exhibited by the anion of 4*H*-dibenzo[*f*,*h*][1,5]dithionin (**15**).

The allyl anions generated from 1,3-(bismethylthio)propene **1a**[4] or from the corresponding bisphenylthio derivative **1b**[5] have been shown to be usefull synthetic equivalents of the β-acyl vinyl anion.[4] As an example, **1a** has been used in a synthesis of racemic prostaglandin $F_{2\alpha}$.[6] We reasoned that the intrinsically chiral allyl anions **2a,b** derived from dibenzo- and 1,1'-dinaphtho-2,2'-dithiopropenes respectively would have represented chiral versions of these reagents with a C_2 symmetry. Here we report on their generation and on their unexpected chemical behavior.

1a R = Me
1b R = Ph

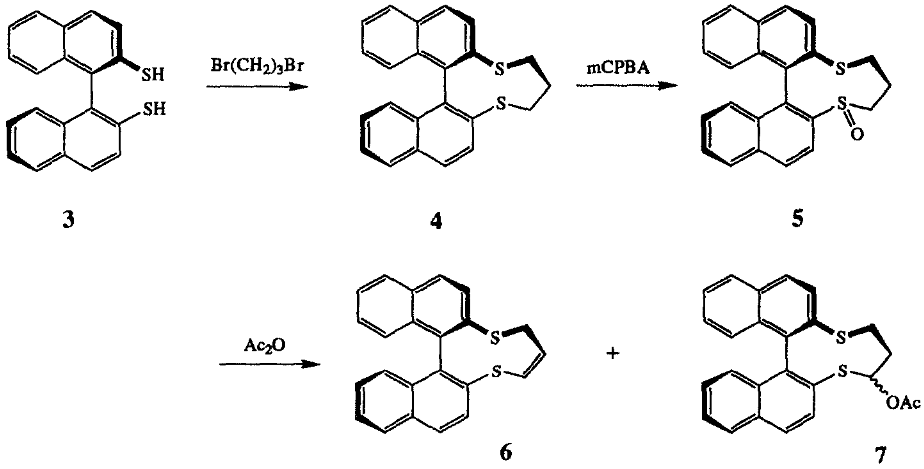


2a



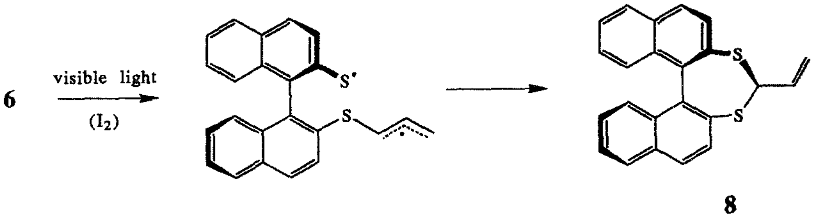
2b

Nucleophilic substitution of 1,3-dibromopropane with 1,1'-dinaphtho-2,2'-dithiol **3** afforded high yield of the dinaphthodithionin **4**[7,8] (98%, 281-2 °C from CH_2Cl_2/*n*-hexane) which was oxidized in high yield to a single diastereomeric sulfoxide **5** [*m*-chloroperbenzoic acid (mCPBA)/ CH_2Cl_2, 95%, 275-6 °C from CH_2Cl_2/*n*-hexane] as shown in equation 1. The total diastereoselectivity observed in the oxidation is remarkable considering the size of the ring. The stereochemistry of the sulfinyl oxygen is supposedly pseudoequatorial in analogy with similar sulfoxides.[9] Pummerer reaction[10] of the latter in acetic anhydride afforded the olefin **6**[7] (20%, 241-2 °C from CH_2Cl_2/*n*-hexane) together with a variable amount of the acetate **7** (ca. 40%, mixture of isomers) which could be deacetoxylated to **6** by heating with sodium carbonate.



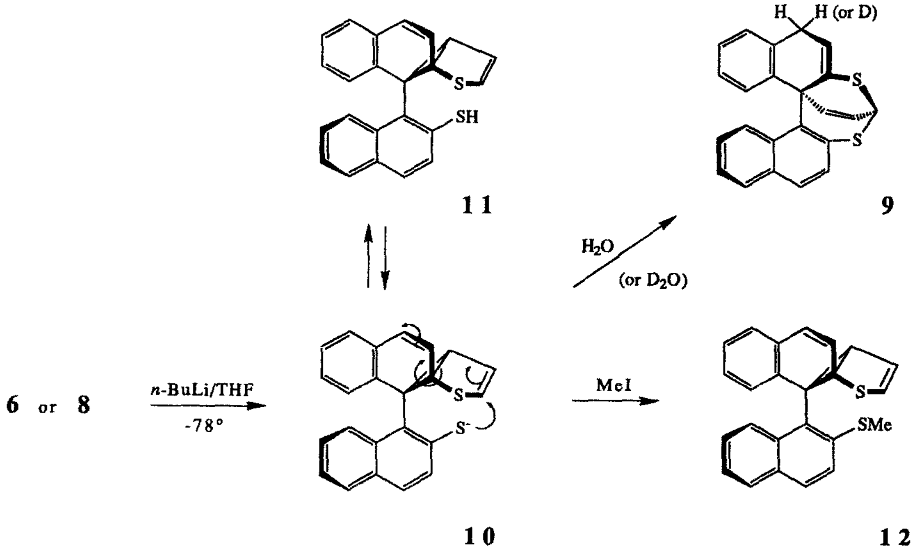
(1)

Olefin **6** rearranged in the presence of light to the isomeric olefin **8**[7] (quantitative, 157-8 °C from CH_2Cl_2/*n*-hexane), probably through radical intermediates as evidenced by the shorter reaction time of the reaction carried out in the presence of iodine as a radical initiator and by the fact that the rearrangement did not occur in the dark (equation 2).



(2)

Generation of the anion **2b** from **6** with *n*-buthyllithium in THF at -78 C°, followed by quenching of the anion with water, did not give back the starting material **6**, as it was expected, but the highly rearranged isomer **9**[11] (90%, 147-8 °C from CH_2Cl_2/*n*-hexane) instead (equation 3). The structure assignement was based on decoupling experiments and other spectroscopic data.[7]



(3)

Quenching of the anion with deuterated water afforded **9** deuterated stereoselectively at the methylenic carbon.

The reaction probably proceeds through the thiolate **10** as intermediate because the thiol **11** was observed in the NMR spectrum of the crude reaction mixture, but it could not be isolated even upon quenching of the reaction mixture with acidic (4.0 pH buffer) water.

More convincingly, quenching of the anion generated from **6** with methyl iodide afforded high yields of **12** (94% yield based on recovered starting material, 190-1 °C from CH_2Cl_2/*n*-hexane) as the sole identifiable product. The structure of **12** was assigned on the basis of an X-ray structure determination (Figure 1).[12]

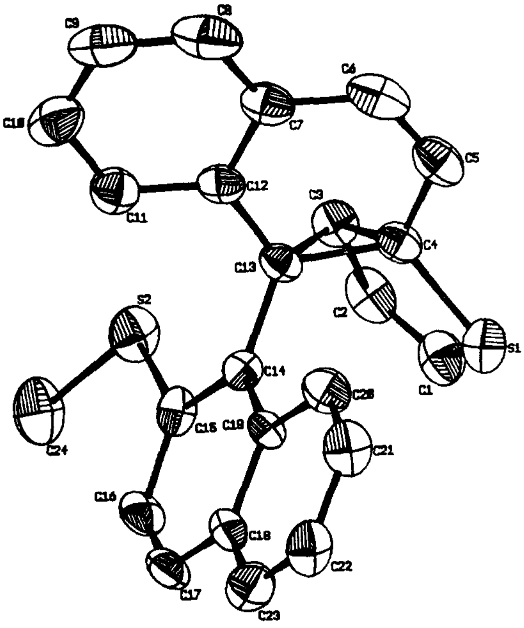
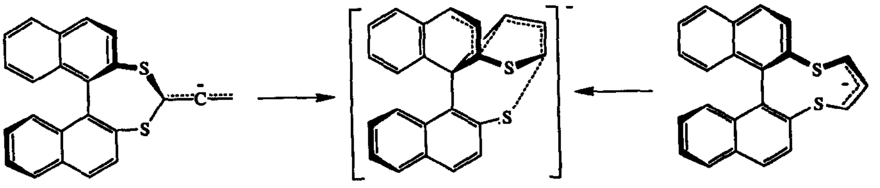


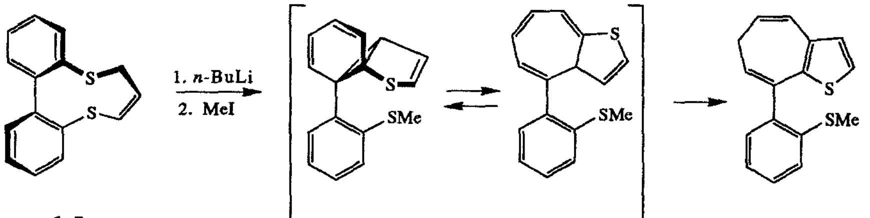
Figure 1. ORTEP representation of compound 12.

The anion **13** generated from **8**, which is also chiral with a C_2-symmetry, rearranged under similar reaction conditions to the same products observed in the reaction of **6**. This observation suggests the formation of a common intermediate in the two reactions and which might be postulated as the extensively delocalized anion shown with structure **14**. The latter may add the electrophile to the sulfur atom (*e.g.* methyl iodide) to deliver **12** or to the distal carbon of anion (*e.g.* H_20 or D_2O) to give **9**. The energy gain for the formation of the anion **14** may be given by release of strain energy and by the formation of a thiolate anion or a planar sulfur substituted allyl anion. Eventually, however, any process leads to loss of aromaticity of one of the naphthyl rings.



13 **14** **2b**

It was reasoned that the allyl anion derived from the biphenyl derivative **15** could be more stable because the degenerative process requires a higher energy of dearomatization. The reaction of biphenyl derivative **15** (85-6 °C from CH_2Cl_2/*n*-hexane) with *n*-butyllithium (equation 4) followed by quenching with methyl iodide afforded product **16** (90% yield based on recovered starting material, 104-5 °C from CH_2Cl_2/*n*-hexane). This compound is thought to be generated via the norcaradiene - tropylidene structures **17-N** and **17-T** suggesting a similar behaviour with the binaphthyl case illustrated in equation 3.



15 **17-N** **17-T** **16** (4)

On the basis of the results so far obtained, there are no evidencies of charge delocalization in the allyl anions **2a,b** probably because the peculiar geometry of the molecules under investigation precludes a correct orbital allignment of the allyl system. It should be recalled, however, that deprotonation of the related system and lower vinylogous 5*H*-1,4-dithiepin was also reported not to occurr at the allyl position.[13]

References and Notes

1. Work carried out in the frame of "Progetto Finalizzato Chimica Fine e Secondaria II" of C.N.R. (Rome).
2. Present address: Dipartimento di Chimica, Università di Venezia, Dorsoduro 2137, I-30123 Venezia, Italy.
3. Author to whom inquiries concerning the X-ray structure determination should be directed.
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6. Corey, E. J.; Noyori, R. *Tetrahedron Lett.* **1970**, 311.
7. All new compouds presented correct elemental composition and were characterized by ^{1}H-NMR (300 MHz) and other spectroscopic techniques. **6**: ^{1}H-NMR ($CDCl_3$) δ 2.74-2.80 (1H, m), 3.18-3.26 (1H, m), 5.34-5.46 (2H, m), 7.03-7.05, 7.25-7.32, 7.44-7.55, 7.59-7.62, 7.80-7.98 (12H, series of m, Ar); IR (KBr) 3040, 1495, 1395, 810, 715. **8**: ^{1}H-NMR ($CDCl_3$) δ 5.06 (1H, d, J = 9.9 Hz), 5.21 (1H, d, J = 16.8 Hz), 5.32 (1H, d, J = 9.0 Hz), 5.87 (1H, ddd, J = 16.8, 9.9, 9.0 Hz), 6.90-8.10 (10H, m, Ar); IR (KBr) 3030, 1623, 1576, 1317, 1158, 823, 755. **9**: ^{1}H-NMR ($CDCl_3$) δ 3.79 (1H, dd, J = 18.0, 4.2 Hz), 3.90 (1H, dd, J = 18.0, 3.3 Hz), 5.68 (1H, dd, J = 9.3, 3.0 Hz), 6.06 (1H, d, J = 9.3 Hz), 6.85 (1H, dd, J = 4.2, 3.3 Hz), 7.05-7.65 (10H, series of m, Ar); IR (KBr) 3049, 2923, 1617, 1506, 812, 740, 671. **12**: ^{1}H-NMR ($CDCl_3$) δ 2.15 (1H, d, J = 2.7 Hz), 2.57 (3H, s), 5.54 (1H, d, J = 5.7 Hz), 6.07 (1H, dd, J = 5.7, 2.7 Hz), 6.42 (1H, d, J = 10.0 Hz), 6.54 (1H, d, J = 10.0 Hz), 6.92-7.46, 7.63-7.92 (10H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ 17.30, 33.99, 44.34, 52.65, 120.90, 124.66, 124.87, 125.01, 125.61, 126.92, 127.31, 127.41, 128.24, 129.13, 129.20, 129.22, 129.58, 129.72, 131.15, 132.73, 132.75, 134.21, 137.20, 138.93; IR (KBr) 3070, 2914, 1490, 1302, 1111, 810, 799, 740. **15**: ^{1}H-NMR ($CDCl_3$) δ 2.69 (1H, ddd, J = 12.0, 3.7, 1.0 Hz), 3.22 (1H, t, J = 12.0 Hz), 5.30-5.42 (1H, m), 5.54 (1H, d, J = 9.0 Hz), 7.10-7.50 (7H, m, Ar), 7.65-7.72 (1H, m, Ar); IR (KBr) 3051, 2920, 2900, 1440, 1422, 1350, 754, 742, 714. **16**: ^{1}H-NMR ($CDCl_3$) δ 2.28 (3H, s), 2.54 (2H, bs), 5.50 (1H, t, J = 6.9 Hz), 5.72 (1H, dt, J = 9.6, 6.9 Hz), 6.62 (1H, d, J = 5.1 Hz), 6.83 (1H, d, J = 9.6 Hz), 7.07-7.35 (6H, series of m, Ar); IR (KBr) 3049, 3022, 1605, 1456, 1430, 1073, 1033, 847, 748, 727.
8. Other more direct methods of preparation of **6**, as for example reaction of **3** with propargyl bromide or 1,3-dibromopropene were not succesful. The product obtained was the compound which arises from one mole of **3** and two moles of the alkyl halide even when large excess of the thiol was used.
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10. De Lucchi, O.; Miotti, U.; Modena, G. *Org. React.* **1991**, *40*, 157.
11. Two other compounds produced in ca. 10% yield in the reaction quenched with water have not yet been characterized.
12. Unit cell parameters: a = 27.786(3), b = 7.485(1), c = 17.606(2) Å, β = 102.7(2)°: $C_{24}H_{18}S_2$; mw 370.53; Z = 8; D = 1.38 g/cm^3; monoclinic C2/c; λ (MoKα) = 0.7107Å. The structure was phased by SHELX 86 program and refined by blocked full matrix least squares using SHELX 76 program. The final conventional R factor for the 1446 considered observed reflections [$I \geq 2.7\sigma(I)$] was 0.055.
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