

## Ring-expansion of 3-Arylinden-1-ones with Lithium Methylsulphinylmethanide

Katherine Buggle,\* Úna Ní Ghógáin, and Daniel O'Sullivan  
Department of Chemistry, University College, Dublin

3,4-Disubstituted 1-naphthols (5a—h) are obtained in 49—89% yield by the reaction of 2,3-disubstituted inden-1-ones (1a—h) with lithium methylsulphinylmethanide

2,3-Disubstituted inden-1-ones have been converted into 2,4-disubstituted 1-naphthols by treatment with diazomethane and successive pyrolysis of the dihydropyrazoles and cyclopropanes produced<sup>1,2</sup> (*cf.* ref. 3). We now report on the formation of the isomeric 3,4-disubstituted 1-naphthols by the reaction of 2,3-disubstituted inden-1-ones with lithium methylsulphinylmethanide (dimsyl-lithium).

During an earlier study<sup>2</sup> 2-phenyl-3-phenylthioinden-1-one (1a) was treated with lithium methylsulphinylmethanide to obtain a sample of 2-phenyl-3-(methylsulphinylmethyl)inden-1-one. This reaction yielded a major product identified by spectroscopy as a 1-naphthol which was not reported at the time. Two possible structures for this product were the 3,4-disubstituted 1-naphthol (5a) and the 2,4-disubstituted 1-naphthol (4), the former resulting from reaction of the dimsyl carbanion at C(1) and the latter from reaction at C(3) of the indenone (1a). The second possibility was excluded by synthesis of 2-phenyl-4-phenylthio-1-naphthol (4) according to the Scheme.

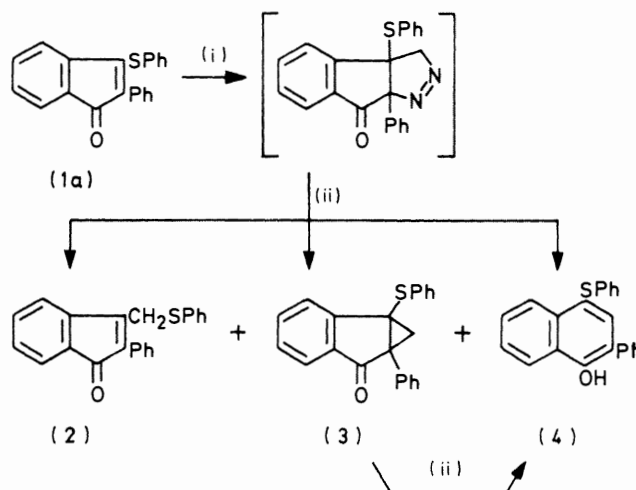
The indenone (1a) on treatment with diazomethane yielded a pyrazoline which was pyrolysed without purification, affording three products; the indenone (2), the cyclopropane (3), and the 1-naphthol (4) (*cf.* ref. 2). The cyclopropane (3) on pyrolysis yielded the 1-naphthol (4). This compound was found to be different from the product of the lithium methylsulphinylmethanide experiment which was therefore assigned structure (5a).

This finding led us to examine the possible ring-expansion of other inden-1-ones with methylsulphinylmethanide anion. The reaction was applied to a series of 3-arylidene-1-ones (1b—h). These reactions gave, in each case, a mixture of the 1-naphthol (5b—h) and the  $\beta$ -hydroxy sulphoxide (6b—h), the relative yields of which depended upon the reaction time. The yields of naphthols (5) obtained with a reaction time of 24 h are given in Table 1. The yields of  $\beta$ -hydroxy sulphoxides (6) were 20—50% after 1 h.

Both the 1-naphthols (5) and  $\beta$ -hydroxy sulphoxides (6) were unstable compounds which deteriorated with time, and difficulty was experienced in purifying them for elemental analysis. Analytical figures were obtained either for the 1-naphthols (5d, f, and h) and (4) or their acetates (7a, c, and e) with the exception of the naphthyl derivative (7g) for which only an accurate mass was obtained.

Mass spectra of the  $\beta$ -hydroxy sulphoxides showed complex patterns of fragmentation. The spectrum of the diphenyl derivative (6b) showed a molecular ion of low abundance (8%), a base peak at  $m/z$  299 ( $M^+ - 61$ ), and a significant peak at  $m/z$  282 ( $M^+ - 78$ , 80%). The spectra of the other  $\beta$ -hydroxy sulphoxides (6c—h) similarly showed a molecular ion of low relative intensity (<10%) and a base peak at either  $m/z$   $M^+ - 61$  or  $M^+ - 78$ .

The n.m.r. spectra of the 1-naphthols (5b—h), like that of 1-naphthol itself, show a multiplet at  $\delta$  ca. 8.34 for (8)H which is absent in the spectrum of 2-naphthol; in the case of the 4-phenylthionaphthols (4) and (5a) the multiplet at  $\delta$  8.34 integrates for two protons [(8)- and (5)-H].



Scheme. Reagents and conditions: (i) CH<sub>2</sub>N<sub>2</sub>; (ii) heat

While fluoren-9-one has been ring-enlarged with diazomethane<sup>4</sup> the reaction with lithium methylsulphinylmethanide gave only the  $\beta$ -hydroxy sulphoxide (8).<sup>5</sup> Reaction of the 2,3-diarylidene-1-ones (1b and d) with dimethylsulphonium methylide proceeded normally giving the epoxides (9) and (10) rather than ring-enlarged products.

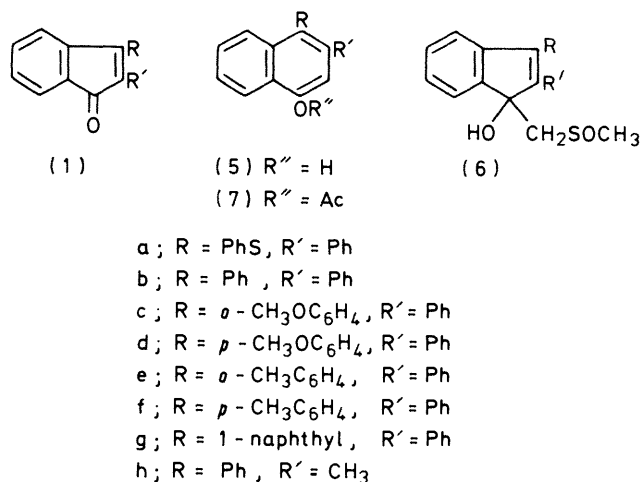
### Experimental

<sup>1</sup>H N.m.r. spectra were obtained at 60 MHz in CDCl<sub>3</sub> with SiMe<sub>4</sub> as internal reference. Merck silica gel was used for t.l.c. Analytical data are given in Table 2. The  $\beta$ -hydroxy sulphoxide (6d), m.p. 164—166 °C (decomp.) was identified by mass- and i.r.-spectroscopy but was not further characterised.

*Reaction of Inden-1-ones (1) with Methylsulphinylmethanide.*—n-Butyl-lithium (1.6M in hexane; 4 ml) was added to dimethyl sulphoxide (DMSO) (10 ml) stirred under nitrogen. After 30 min the inden-1-one (1) (500 mg) was added and the reaction mixture was stirred for 1 h or 24 h. The mixture was acidified with dilute hydrochloric acid (10%), added to water, and extracted into chloroform. The extract was washed with water, dried, and concentrated. The residue was purified by t.l.c. with chloroform as eluant for the 1-naphthols and ethyl acetate for the  $\beta$ -hydroxy sulphoxides.

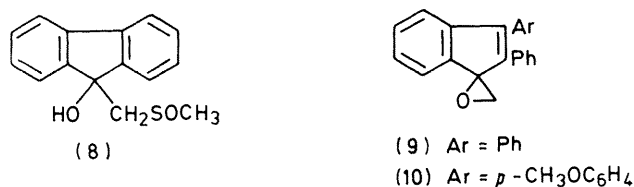
Fluoren-9-one treated as above for 24 h gave the  $\beta$ -hydroxy-sulphoxide (8) (75%) as needles, m.p. 148—150 °C (decomp.) (lit.,<sup>5</sup> 156—157 °C);  $m/z$  258;  $\delta$  2.64 (3 H, s) and 3.21 (2 H, q, J 13 Hz).

In one experiment with 2,3-diphenylinden-1-one (1b) chloroform was added to the reaction mixture before the addition of hydrochloric acid. This reaction yielded, in addition to the 1-naphthol (5b), *di*-(3,4-diphenyl-1-naphthyl)



**Table 1.** Reaction of 2,3-disubstituted inden-1-ones (1a—h) with lithium methylsulphinylmethanide for 24 h to give the corresponding 1-naphthols (5a—h)

| Starting indenone (1) suffix letter | Product 1-naphthol (5) yield (%) |
|-------------------------------------|----------------------------------|
| (a)                                 | 61                               |
| (b)                                 | 68                               |
| (c)                                 | 50                               |
| (d)                                 | 89                               |
| (e)                                 | 49                               |
| (f)                                 | 53                               |
| (g)                                 | 52                               |
| (h)                                 | 63                               |



carbonate, m.p. 223—224 °C;  $m/z$  618; (Found: C, 82.95; H, 4.65.  $\text{C}_{45}\text{H}_{30}\text{O}_3$  requires C, 82.97; H, 4.39%);  $\nu_{\text{C=O}}$  1790  $\text{cm}^{-1}$ .

**2-Phenyl-4-phenylthio-1-naphthol** (4).—Ethereal diazomethane (6-fold excess) was added to a solution of 2-phenyl-3-phenylthioinden-1-one (1a) (328 mg) in diethyl ether (10 ml) and the stoppered reaction flask was kept for 28 h. Evaporation of the solvent afforded an oil which was heated at 120 °C/24 mmHg for 20 min and then separated by t.l.c. with chloroform as eluant. The band of highest  $R_F$ -value gave the 1-naphthol (4) (18 mg, 5.3%). The next band was the indenone (2), an oil (52 mg, 15.4%),  $\nu_{\text{max}}$  1700  $\text{cm}^{-1}$  (C=O);  $\delta$  7.46 (14 H, m) and 4.2 (2 H, s), which was characterised as the sulphone, m.p. 142—143 °C (from diethyl ether);  $\nu$  1700, 1320, and 1155  $\text{cm}^{-1}$  (Found: C, 72.95; H, 4.3.  $\text{C}_{22}\text{H}_{16}\text{O}_3\text{S}$  requires C, 73.32; H, 4.48%). The third band gave 1a,6a-dihydro-6a-phenyl-1a-phenylthiocycloprop[ $\alpha$ ]inden-6(1H)-one (3) as an oil (220 mg, 65%),  $\nu_{\text{max}}$  3080 and 1720  $\text{cm}^{-1}$ ;  $\delta$  7.63 (14 H, m) and 2.43 (2 H, q,  $J$  5.4 Hz). This compound on pyrolysis gave the naphthol (4) (156 mg, 71%).

**Table 2.**

| Compound | M.p. (°C)            | Formula   | Found (%) (Required) |            |              |
|----------|----------------------|---|----------------------|------------|--------------|
|          |                      |   | C                    | H          | S            |
| (4)      | 128—129              | $\text{C}_{22}\text{H}_{16}\text{OS}$               | 80.55<br>(80.5)      | 4.8<br>4.9 | 9.5<br>9.75  |
| (5b)     | 142—143 <sup>a</sup> |   |                      |            |              |
| (5d)     | 184—185              | $\text{C}_{23}\text{H}_{18}\text{O}_2$              | 84.5<br>(84.6)       | 5.9<br>5.6 |              |
| (5f)     | 129—130              | $\text{C}_{23}\text{H}_{18}\text{O}$                | 89.1<br>(89.0)       | 5.6<br>5.8 |              |
| (5h)     | 97—99                | $\text{C}_{17}\text{H}_{14}\text{O}$                | 86.8<br>(87.15)      | 6.1<br>6.0 |              |
| (6b)     | 185—187 <sup>b</sup> | $\text{C}_{23}\text{H}_{20}\text{O}_2\text{S}$      | 76.7<br>(76.65)      | 6.0<br>5.6 | 9.2<br>8.9   |
| (6c)     | 173—174 <sup>b</sup> | $\text{C}_{24}\text{H}_{22}\text{O}_3\text{S}$      | 73.5<br>(73.8)       | 5.8<br>5.7 | 8.4<br>8.2   |
| (6e)     | 156—158 <sup>b</sup> | $\text{C}_{24}\text{H}_{22}\text{O}_2\text{S}$      | 76.7<br>(77.0)       | 6.2<br>5.9 | 8.2<br>8.6   |
| (6f)     | 152—153 <sup>b</sup> | $\text{C}_{24}\text{H}_{22}\text{O}_2\text{S}$      | 76.45<br>(77.0)      | 5.7<br>5.9 | 9.2<br>8.6   |
| (6g)     | 177—178 <sup>b</sup> | $\text{C}_{27}\text{H}_{22}\text{O}_2\text{S}$      | 79.0<br>(79.0)       | 5.6<br>5.4 | 8.0<br>7.8   |
| (6h)     | 150—152 <sup>b</sup> | $\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}$      | 72.5<br>(72.45)      | 5.8<br>6.1 | 10.8<br>10.7 |
| (7a)     | 150—151              | $\text{C}_{24}\text{H}_{15}\text{O}_2\text{S}$      | 78.2<br>(77.8)       | 5.0<br>4.9 | 8.3<br>8.6   |
| (7b)     | 163—164 <sup>c</sup> |   |                      |            |              |
| (7c)     | 99—101               | $\text{C}_{25}\text{H}_{20}\text{O}_3$              | 81.3<br>(81.5)       | 5.7<br>5.5 |              |
| (7e)     | 105—106              | $\text{C}_{25}\text{H}_{20}\text{O}_2$              | 85.5<br>(85.2)       | 5.5<br>5.7 |              |
| (7g)     | 161—162              | $\text{C}_{28}\text{H}_{20}\text{O}_2$ <sup>d</sup> |                      |            |              |

<sup>a</sup> Ref. 1 gives m.p. 142—143 °C; ref. 6 gives m.p. 143—144 °C.

<sup>b</sup> Previous decomposition. <sup>c</sup> Ref. 6 gives m.p. 162—162.5 °C.

<sup>d</sup> Accurate mass correct to 2.1 mmu (388.1484).

**2,3-Diphenylspiro[indene-1,2'-oxirane]** (9).—Sodium hydride (0.068 g; 60% dispersion in oil) was added to DMSO (15 ml) and the mixture was heated at 70—75 °C for 45 min. The cooled mixture was diluted with tetrahydrofuran (15 ml) and treated at 0 °C with a solution of trimethylsulphonium iodide (0.28 g) in DMSO (5 ml). After 1 min 2,3-diphenylinden-1-one (1b) (400 mg) was added and the resulting mixture was stirred at 0 °C for a few minutes and then at room temperature for 1 h. The solution was diluted with water, extracted three times with chloroform, and the extracts were washed with saturated aqueous sodium chloride, dried, and concentrated. The residue was solidified by trituration with diethyl ether and was crystallised from methanol to give the spiro compound (9) as yellow needles (308 mg, 73%), m.p. 120—121 °C (lit.<sup>1</sup> 120—122 °C);  $\delta$  3.17 (2 H, q,  $J$  6 Hz).

3-(*p*-Methoxyphenyl)-2-phenylinden-1-one (1d) in a similar reaction gave the unstable oxirane (10) as pale yellow needles, m.p. 134—135 °C (Found: C, 85.2; H, 5.35.  $\text{C}_{23}\text{H}_{18}\text{O}_2$  requires C, 84.64; H, 5.56%);  $m/z$  326.1.

## References

- B. Eistert and W. Mennicke, *Chem. Ber.*, 1967, **100**, 3495.
- K. Buggle and D. O'Sullivan, *J. Chem. Soc., Perkin Trans. I*, 1975, 572.
- C. F. Koelsch, *J. Org. Chem.*, 1961, **26**, 1003.
- B. Eistert and M. A. El-Chahawi, *Monatsh. Chem.*, 1967, **98**, 941.
- G. A. Russell, E. G. Janzen, M.-D. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, 1962, **84**, 2652.
- L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, 1939, **61**, 2619.

Received 13th January 1983; Paper 3/047