ALIPHATIC CHEMISTRY OF FLUORENE

PART VIII. BENZYL 9-FLUORENYL SULPHOXIDE AND SOME 9-FLUORENYL SULPHIDES

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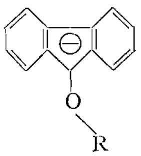
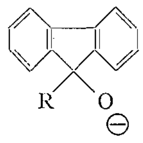
ABSTRACT

Allyl 9-fluorenyl sulphide, benzyl 9-fluorenyl sulphide, and di-9-fluorenyl sulphide are stable to boiling ethereal phenyl lithium, in marked contrast to the corresponding ethers. Benzyl 9-fluorenyl sulphoxide has been prepared and shown to be more weakly acidic than 9-fluorenyl sulphones.

Wittig and co-workers have reported (1) that the anions (I) derived from certain 9-fluorenyl ethers rearrange to the corresponding 9-substituted-9-fluorenyl alkoxides (II). Of particular interest to the present study were the anions of the allyl and benzyl ethers (I, R = $CH_2CH{=}CH_2$ and $C_6H_5CH_2$, respectively) which rearranged very rapidly at $-10°$. The anion of di-9-fluorenyl ether rearranged at room temperature but those of other alkyl and aryl ethers required elevated temperatures and longer reaction times.



I



II

These reactions belong to a wider group known as the Stevens rearrangement (2, pp. 527–528; 3, pp. 282–283; 4). Most of the published work has been concerned with ethers (1, 5, 6, 7, 8) but Hauser and co-workers have examined some sulphides (4). Both benzyl methyl sulphide and dibenzyl sulphide underwent the Stevens rearrangement, more typical of the reactions of quaternary ammonium compounds. Similar rearrangements have been reported for some sulphonium compounds (4, 9). Although allylamine-N-oxides show allylic rearrangement from nitrogen to oxygen (10, 11), related allyl (12) and benzyl (4) sulphoxides and sulphones do not rearrange. Allyl phenyl sulphide and allyl *p*-tolyl sulphide possibly undergo the ortho Claisen rearrangement (13; cf. ref. 14) but more slowly than the corresponding ethers. Unlike the ether, *t*-butyl phenyl sulphide does not rearrange when distilled (15, 16).

We have now prepared by a general method (17) allyl 9-fluorenyl sulphide, benzyl 9-fluorenyl sulphide, and di-9-fluorenyl sulphide. All three sulphides dissolved in ethereal solutions of phenyl lithium with formation of the deep red color associated with fluorene anions of this type (1, 18) but the color was apparently unchanged after boiling under reflux for up to 24 hours. Hydrolysis with water regenerated the original sulphides. Thus the anions of the sulphides are more stable than those of the ethers, resembling the 9-fluorenyl-trialkylammonium compounds in not undergoing the ortho rearrangement (19).

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The color of the anion derived from benzyl 9-fluorenyl sulphide was almost immediately discharged by the addition of methyl iodide. Oxidation of the tertiary sulphide gave benzyl 9-methyl-9-fluorenyl sulphone, isomeric with the product of benzylation of methyl 9-fluorenyl sulphone. The non-identity of the two sulphones confirmed that rearrangement of benzyl 9-fluorenyl sulphide anion had not occurred.

Allyl 9-fluorenyl sulphide was not obtained crystalline and decomposed on attempted distillation.* Like other allyl sulphides (22, 23) oxidation gave the sulphone without epoxidation of the double bond. Since allyl fluorene-9-carboxylate rearranges to 9-allylfluorene-9-carboxylic acid when heated with lithamide in toluene (24), the reaction of allyl 9-fluorenyl sulphone with sodamide has been examined. Extensive decomposition occurred, these results paralleling those reported by Cope (12) for other sulphones. The infrequency with which allyl and benzyl groups migrate from sulphur to carbon may be due to *d*-orbital resonance diminishing the charge on the potential migration terminus (cf. the effect of sulphur on the stability of anions (20, 21, 24)). Similar reasons have been put forward to account for the failure of thiophenol acetate to undergo the Fries rearrangement (26). A recent paper (27) has described the pyrolysis of some sulphones which resulted in the formation of rearranged hydrocarbons, but probably by a free radical mechanism.

The reaction between fluorene, thionyl chloride, and aluminum chloride has been reported (28) to yield di-9-fluorenyl sulphoxide, characterized by oxidation to di-9-fluorenyl sulphone (m.p. 199° with decomposition). Although one example of intramolecular acylation at the 9-fluorenyl position has been described (29), Friedel–Crafts and related reactions generally give 2-fluorenyl derivatives (30, p. 277). We have now prepared di-9-fluorenyl sulphone by oxidation of the sulphide and find it to have m.p. 242–244° with decomposition. Paucity of experimental details has prevented repetition of Courtot's preparation (28).

Allyl and benzyl 9-fluorenyl sulphides decomposed rapidly at 258–260° with formation of evil-smelling mixtures. The only product identified was di-9-fluorenyl (8–10%). Di-9-fluorenyl sulphide behaved similarly, giving difluorenyl (11%) accompanied by di-9-fluorenylidene (9%). These observations parallel those reported for the corresponding ethers (1).

In an earlier paper (17) the acidity of 9-fluorenyl sulphones was described. We have now prepared benzyl 9-fluorenyl sulphoxide and examined its reactions. (For a recent discussion of the formation of sulphoxides, see ref. 31.) It dissolves in methanol containing sodium methoxide without formation of the yellow color associated with 9-fluorenyl anions of this type (17, 32, 33). Further, the presence of the alkoxide does not significantly affect the ultraviolet spectrum. Addition to the solution of either methyl or allyl halides led to mixtures from which traces of hydrocarbons were isolated. The infrared spectra showed the presence of sulphones, and fluorenone could be isolated as the 2,4-dinitrophenylhydrazone. Failure to isolate alkylation products is probably due to the low acidity of the sulphoxide since, after 1 hour, dilution precipitated unchanged sulphoxide. Alkylation of the related sulphones is known to be rapid (17). Although disappointing, these results were not unexpected. Unlike the corresponding sulphones, sulphoxides are insoluble in aqueous sodium hydroxide solution (34), and dibutyl sulphoxide undergoes hydrogen exchange very slowly in alkaline media (35). It has been concluded from

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**Allylic sulphides are readily isomerized to propenyl sulphides by strong bases (for examples, see refs. 20, 21). In view of the failure of benzyl 9-fluorenyl sulphide anion to undergo rearrangement, the structure of the allyl sulphide was confirmed only by its infrared spectrum (see Experimental).*

spectral and other studies (36) that the electron-accepting properties of the sulphoxide group are only slightly greater than those of the uncharged sulphides. Our results agree with this conclusion.

The infrared spectra of the sulphones reported in this and the earlier paper (17) have been discussed elsewhere (37).

EXPERIMENTAL

Benzyl 9-Fluorenyl Sulphide

Prepared from 9-bromofluorene and benzyl mercaptan in the usual way (17), it crystallized from acetone–methanol as colorless prisms and laths (87%), m.p. 66–67°. Found: C, 83.38; H, 5.80%. Calculated for $C_{20}H_{16}S$: C, 83.26; H, 5.59%.

Benzyl 9-Fluorenyl Sulphoxide

Following a series of trial experiments, the following was found to be reproducible:

The sulphide (2 g) in acetic acid (100 ml) and 50% hydrogen peroxide (15 ml) was heated on the steam bath for 15 minutes. The yellow solution was poured into water, precipitating the *sulphoxide* as a white solid. Crystallization from ethanol gave felted needles (1.45 g), m.p. 147–148° with decomposition to a red liquid. Found: C, 78.55; H, 5.40%. Calculated for $C_{20}H_{16}OS$: C, 78.91; H, 5.30%.

Benzyl 9-Fluorenyl Sulphone

The oxidation described above was continued for 2 hours, additional 50% hydrogen peroxide (10 ml) being added after 1 hour. The *sulphone* formed thick colorless needles from ethanol (82%), m.p. 169–170°. Found: C, 74.64; H, 4.85%. Calculated for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03%.

Benzyl 9-Methyl-9-fluorenyl Sulphide

Benzyl 9-fluorenyl sulphide (1 g) dissolved in ethereal phenyl lithium (from 2 g bromobenzene) with formation of a deep red color, which was not visibly altered after boiling of the solution under reflux for 24 hours. At the end of this period, methyl iodide (2 g) was added, the solution being almost immediately decolorized. After it was washed with ice water, the ether solution was dried (K_2CO_3), divided into two approximately equal parts, and each part evaporated to dryness.

The oil from one part was left under methanol for 4 weeks, crystallization slowly taking place. Recrystallization from methanol gave small colorless prisms (0.26 g), m.p. 59.5–61.0°. Found: C, 83.61; H, 6.29%. Calculated for $C_{21}H_{18}S$: C, 83.40; H, 6.00%.

The oil from the second part was oxidized in the usual way (17) with hydrogen peroxide. *Benzyl 9-methyl-9-fluorenyl sulphone* crystallized from methanol as colorless needles (0.4 g), m.p. 155–156°. Found: C, 75.66; H, 5.32%. Calculated for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.42%. The same compound (m.p., mixed m.p., and identity of infrared spectra) was obtained by methylating benzyl 9-fluorenyl sulphone in the usual way (17).

Benzylation of 9-fluorenyl methyl sulphone (17) gave *9-benzyl-9-fluorenyl methyl sulphone*, crystallizing from acetone as lustrous plates (69%), m.p. 172–173°, depressed to 141–153° by addition of benzyl 9-methyl-9-fluorenyl sulphone. Found: C, 75.03; H, 5.32%. Calculated for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.42%.

Di-9-fluorenyl Sulphone

9-Fluorenyl mercaptan (10 g) (38) and 9-bromofluorene (13 g) were dissolved in hot ethanol (500 ml). The addition of a solution of sodium methoxide (from 1.2 g sodium) in methanol (50 ml) brought about a vigorous reaction. The *sulphide* started to separate almost at once. Recrystallization from xylene gave colorless lustrous plates (16.5 g, 82%), m.p. 257–259° with decomposition to a red liquid.

Oxidation of the sulphide (1 g) in hot acetic acid (1500 ml) with 50% hydrogen peroxide (15 ml) gave the *sulphone*, which crystallized from xylene as almost colorless prisms (0.7 g), m.p. 242–244° with partial decomposition. Found: C, 78.85; H, 4.43%. Calculated for $C_{26}H_{18}O_2S$: C, 79.16; H, 4.60%.

Allyl 9-Fluorenyl Sulphone

The reaction between 9-bromofluorene (24.5 g), allyl mercaptan (10 g), and sodium methoxide (from 2.5 g sodium) in methanol (250 ml) gave the sulphide as an oil (18 g). It was not obtained crystalline but oxidation in the usual way (17) gave the sulphone (15.2 g) as prisms or plates from acetone–methanol, m.p. 120–121°. Found: C, 70.75; H, 5.23%. Calculated for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22%.

The sulphide was also obtained as an oil from the reaction between 9-fluorenyl mercaptan and allyl chloride.

9-Allyl-9-fluorenyl Methyl Sulphone

Prepared from 9-fluorenyl methyl sulphone in the usual way (17), it crystallized as elongated prisms from acetone, m.p. 168–169°. Found: C, 71.49; H, 5.33%. Calculated for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67%.

Pyrolysis of the Sulphides

Di-9-fluorenyl sulphide (2 g) was placed in a 100-ml Erlenmeyer flask, closed with a cotton plug, and maintained at 258–260° (oil bath) for 2 minutes. Crystallization from heptane gave colorless needles (0.2 g, 11%), m.p. 245–246° after two crystallizations. Comparison with an authentic specimen (39) showed the product to be di-9-fluorenyl. The mother liquors slowly formed a crust of red crystals, which were removed and crystallized from carbon tetrachloride – ethanol. The resulting red needles (0.16 g, 9%) had m.p. 185–186° and were identified as di-9-fluorenylidene by comparison with an authentic specimen (39).

The characteristic sulphone bands in the infrared spectra have been discussed elsewhere (37). The structure of allyl 9-fluorenyl sulphide was supported by strong bands at 989 and 912 cm^{-1}, indicative (40) of the vinyl group.

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