ALIPHATIC CHEMISTRY OF FLUORENE

PART IV. PREPARATION AND ALKYLATION OF SOME SULPHIDES AND SULPHONES[1]

P. M. G. BAVIN[2]

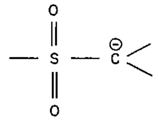
ABSTRACT

The preparations are described of some 9-fluorenyl sulphides which have been oxidized with peracetic acid to the corresponding sulphones.

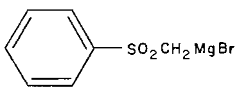
9-Fluorenyl *p*-tolyl sulphone has been alkylated with a range of alkyl halides; other sulphones, including 2-nitro-9-fluorenyl *p*-tolyl sulphone, have been methylated.

Methyl fluorene-9-carboxylate anion was reduced by *p*-toluenesulphonyl chloride to dimethyl 9,9′-difluorenyl-9,9′-dicarboxylate.

The acidity of methylene hydrogen activated by the sulphone group has been known for some time, but opinions have been divided on the reasons. Recent studies by Doering and his co-workers (1, 2, 3) have established that anions of type I are resonance stabilized by overlap between carbon 2*p* and sulphur 3*d* orbitals. The spectroscopic studies of Fehnel and Carmack (4) lend strong support to these conclusions. The latter workers found no evidence for the formation of anions from methylene activated only by a sulphone group, but Grignard derivatives of dialkyl sulphones (5, 6) and aralkyl sulphones (7, where references are given to prior publications) are well known. Field, Holsten, and Clark (7) have recently examined some reactions of phenylsulphonylmethyl magnesium bromide (II) and shown that it was alkylated in modest yield by benzyl chloride and hexyl *p*-toluenesulphonate, in low yield by benzhydryl chloride, and not at all by *t*-butyl chloride and hexyl iodide, results which prompted its formulation as a weakly nucleophilic Grignard reagent rather than as a carbanion salt.

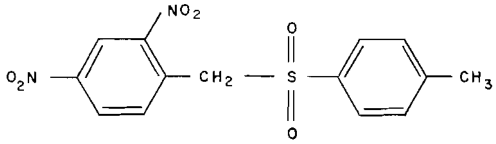


I



II

Nitrobenzyl sulphones are more acidic than the unsubstituted sulphones, and 2,4-dinitrobenzyl *p*-tolyl sulphone (III) has been methylated (8) using potassium ethoxide as base. The only simple sulphone to have been alkylated under comparable conditions is ethyl 9-fluorenyl sulphone (IV) (9).



III

The remarkable facility with which methyl fluorene-9-carboxylate anion reacts with a wide range of alkyl halides (10, 11, 12) has prompted an examination of other 9-substituted fluorenes. Some experiments with 9-benzoylfluorene have already been reported (13). The present paper describes the alkylation of 9-fluorenyl *p*-tolyl sulphone (VII),

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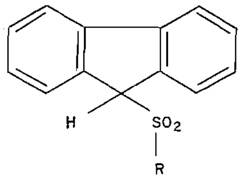
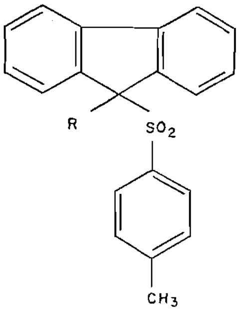
[1] *Manuscript received February 5, 1960.*
Contribution from the Chemistry Department, the University, Hull, East Yorkshire, England.
[2] *I.C.I. Fellow.*



IV, R = CH_3CH_2
V, R = CH_3
VI, R = C_6H_5
VII, R = *p*-$CH_3 \cdot C_6H_4$

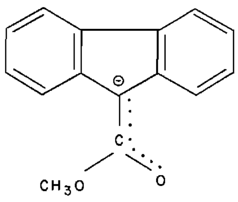
prompted by the work on ethyl 9-fluorenyl sulphone mentioned above (9), together with miscellaneous experiments on related systems.

9-Fluorenyl *p*-tolyl sulphone dissolved in warm ethanol containing sodium ethoxide with formation of a yellow solution. Under similar conditions 2-nitro-9-fluorenyl *p*-tolyl sulphone gave a purple-brown solution, similar to those reported for methyl 2-nitrofluorene-9-carboxylate (14) and 2,4-dinitrobenzyl *p*-tolyl sulphone (8). These solutions undoubtedly contained the organic anions and, in confirmation of this, 9-methyl-, -ethyl-, -isopropyl-, -allyl-, -benzyl-, and -cyclohexyl-9-fluorenyl *p*-tolyl sulphones (VIII, R = alkyl) were prepared by reaction with appropriate alkyl halides. In a similar manner were prepared 9-methyl-2-nitro-9-fluorenyl *p*-tolyl sulphone, 9-methyl-9-fluorenyl phenyl sulphone, and the methyl and isopropyl derivatives of 9-fluorenyl methyl sulphone. Comparison of these results with those reported for phenylsulphonylmethyl magnesium bromide (7) shows that anions of the type X are powerful nucleophiles which behave as true anion metal salts.

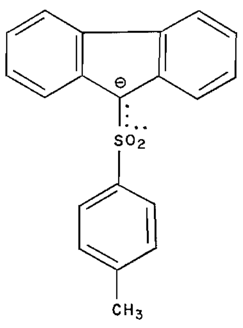


VIII

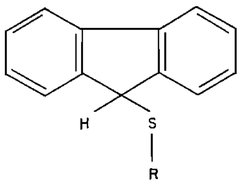
Fluorene has not been alkylated using ethanolic sodium ethoxide as base, so the reactions described above establish that fluorene anion is stabilized by a sulphone group. Although the anions derived from 9-fluorenyl *p*-tolyl sulphone, methyl fluorene-9-carboxylate, and 9-benzoylfluorene show many similar reactions, there are important differences. The sulphone (VII) was recovered unchanged after attempted bromination in acetic acid in the presence of sodium acetate, conditions which gave good yields of methyl 9-bromofluorene-9-carboxylate (11). From the reaction between *t*-butyl chloride and the anion of VII, only unreacted sulphone (30%) was isolated in a pure state. However, examination of the infrared spectrum of the crude product showed the presence of one or more additional compounds, with bands in the positions reported (15) for the *t*-butyl group (cf. methyl 9-*t*-butylfluorene-9-carboxylate (11)). Prolonged reaction times led to the formation of fluorenone, probably by anionic oxidation (16). It follows that the ester anion (IX) is more nucleophilic than the sulphone anion (X), differences in their behavior towards *t*-butyl chloride being of degree rather than kind.



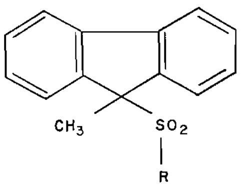
IX



X



XI, R = CH_3
XII, R = C_6H_5
XIII, R = *p*-$CH_3C_6H_4$



XIV, R = CH_3
XV, R = C_6H_5
XVI, R = *p*-$CH_3C_6H_4$

The sulphides (XI, XII, and XIII) have been prepared, the first from 9-fluorenylmercaptan and the others from thiophenol and thio-*p*-cresol, respectively. Methylation with ethereal methyl lithium – methyl iodide (cf. fluorene (17)) gave the tertiary sulphides (XIV, XV, and XVI), the mild conditions employed precluding the rearrangement observed for some 9-fluorenyl ethers (18). All six sulphides were oxidized with peracetic acid to the corresponding sulphones, confirming the structures of the methylation products of sulphones (V, VI, and VII). Attempts were made to oxidize 9-fluorenyl *p*-tolyl sulphide to the sulphoxide but mixtures were always obtained, consisting of the desired sulphoxide together with the sulphone and fluorenone, as shown by infrared spectra.

9-Methyl-9-fluorenyl *p*-tolyl sulphone was not cleaved by sodium piperidide (19, 20), although 9-methylfluorene was slowly formed by reaction with caustic soda in boiling diethylene glycol (cf. 21).

Characteristic sulphone bands have been recorded for the compounds reported in this paper but, being more complex than those reported for other sulphones (15), are being discussed elsewhere (22).

Although keto-esters have been prepared from fluorene-ester anion with acetyl (10) and benzoyl (28) chlorides, the similar reaction with *p*-toluenesulphonyl chloride gave dimethyl 9,9′-difluorenyl-9,9′-dicarboxylate by reductive dimerization of the anion.

EXPERIMENTAL

Sulphides

9-Fluorenylmercaptan (9) was prepared from 9-bromofluorene (23) via the thiouronium salt. Methylation with methyl iodide – methanolic sodium methoxide gave *9-fluorenyl methyl sulphide*, which crystallized from methanol as large colorless blades (77%), m.p. 47–48°. Found: C, 79.42; H, 5.92%. Calc. for $C_{14}H_{12}S$: C, 79.20; H, 5.65%.

9-Fluorenyl phenyl sulphide was prepared by warming 9-bromofluorene (1 mole) and thiophenol (1.1 moles) with methanol containing sodium methoxide (1 mole).* The reaction was complete in 10 minutes. The product crystallized as blades (69%) from methanol, m.p. 48–49°. Found: C, 83.10; H, 4.97%. Calc. for $C_{19}H_{14}S$: C, 83.17; H, 5.14%.

Prepared in a similar way, *9-fluorenyl p-tolyl sulphide* formed laths or dense prisms from ethanol (88%), m.p. 85–86°. Found: C, 83.20; H, 5.43%. Calc. for $C_{20}H_{16}S$: C, 83.29; H, 5.59%.

The foregoing sulphides were methylated with ethereal methyl lithium – methyl iodide, as described for fluorene (17), giving the following:

Methyl 9-methyl-9-fluorenyl sulphide crystallized as rhombohedral plates from methanol (71%), m.p. 63–65°. Found: C, 79.47; H, 6.19%. Calc. for $C_{15}H_{14}S$: C, 79.60; H, 6.23%.

9-Methyl-9-fluorenyl phenyl sulphide formed colorless needles from ethanol after cooling to and keeping at 0° (65%), m.p. 39.5–41.5°. Found: C, 83.30; H, 5.49%. Calc. for $C_{20}H_{16}S$: C, 83.26; H, 5.59%.

9-Methyl-9-fluorenyl p-tolyl sulphide formed well-defined prisms from acetone–methanol, m.p. 72–73° (82%). Found: C, 83.08; H, 5.83%. Calc. for $C_{21}H_{18}S$: C, 83.40; H, 5.60%.

Sulphones

The six sulphides described in the preceding section were oxidized with 50% hydrogen peroxide (1 volume) in acetic acid (3 volumes). The reactions, which were exothermic, were complete in a few minutes at 50°. Yields varied from 72 to 88% (24, 25).

9-Fluorenyl methyl sulphone formed long white needles from methanol or acetic acid, m.p. 188–189°. Found: C, 68.76; H, 5.09%. Calc. for $C_{14}H_{12}O_2S$: C, 68.87; H, 4.95%.

Methyl 9-methyl-9-fluorenyl sulphone crystallized from hexane as colorless prisms or needles, m.p. 136–137°. Found: C, 69.85; H, 5.77%. Calc. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46%.

9-Fluorenyl phenyl sulphone formed colorless prisms from acetone–heptane, m.p. 182–183°. Found: C, 74.34; H, 4.45%. Calc. for $C_{19}H_{14}O_2S$: C, 74.48; H, 4.61%.

9-Methyl-9-fluorenyl phenyl sulphone crystallized as plates from ethanol, m.p. 165–167°. Found: C, 74.30; H, 4.94%. Calc. for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03%.

9-Fluorenyl p-tolyl sulphone crystallized as plates from benzene, m.p. 226–228°, identical with an authentic sample (21).

9-Methyl-9-fluorenyl p-tolyl sulphone formed colorless prisms from benzene–heptane, m.p. 151–152°. Found: C, 75.34; H, 5.26%. Calc. for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.42%.

Attempts to oxidize 9-fluorenyl *p*-tolyl sulphide to the sulphoxide by standard techniques (25, 26) gave mixtures, not resolved by chromatography.

9-Fluorenyl *p*-tolyl sulphone, used in the alkylation experiments described below, was obtained from the reaction between 9-bromofluorene and sodium *p*-toluenesulphinate (21, 29). Prepared similarly, *2-nitro-9-fluorenyl p-tolyl sulphone* (from 9-bromo-2-nitrofluorene (27)) formed almost colorless plates from benzene, m.p. 217–219° with de-

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**It is important to have present a slight excess of thiophenol over alkoxide to prevent formation of difluorenylidene.*

composition. The first crystallization required judicious separation from traces of dinitrodifluorenylidenes. Found: C, 65.70; H, 4.16%. Calc. for $C_{20}H_{15}NO_4S$: C, 65.74; H, 4.14%.

9-Fluorenyl *p*-tolyl sulphone (1 g) was dissolved in ethanol (200 ml) containing sodium ethoxide (from sodium, 0.5 g). The alkyl halide (2–3 g) was added and the mixture was left at room temperature overnight.

9-Methyl-9-fluorenyl p-tolyl sulphone, prepared in this way (81%), crystallized as prisms from hexane, m.p. 150–151°, identical with the sample described above.

9-Ethyl-9-fluorenyl p-tolyl sulphone (76%) formed clusters of long blades from methanol, m.p. 168–169°. Found: C, 75.73; H, 5.81%. Calc. for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.79%.

9-isoPropyl-9-fluorenyl p-tolyl sulphone (75%) crystallized as needles from heptane, m.p. 181–182°. Found: C, 76.27; H, 6.04%. Calc. for $C_{23}H_{22}O_2S$: C, 76.21; H, 6.12%.

9-Allyl-9-fluorenyl p-tolyl sulphone (89%) formed prisms from heptane, m.p. 175–176°. Found: C, 76.78; H, 5.54%. Calc. for $C_{23}H_{20}O_2S$: C, 76.63; H, 5.59%.

9-Benzyl-9-fluorenyl p-tolyl sulphone (86%) formed well-defined prisms from heptane, m.p. 201–202°. Found: C, 78.99; H, 5.51%. Calc. for $C_{27}H_{22}O_2S$: C, 78.99; H, 5.40%.

9-cycloHexyl-9-fluorenyl p-tolyl sulphone (77%) crystallized as small colorless prisms from heptane, m.p. 209–210°. Found: C, 77.87; H, 6.82%. Calc. for $C_{26}H_{26}O_2S$: C, **77.57**; H, 6.51%.

The following were also prepared:

9-Methyl-2-nitro-9-fluorenyl p-tolyl sulphone (81%) formed pale yellow prisms from benzene–hexane, m.p. 187–188°. Found: C, 66.28; H, 4.46%. Calc. for $C_{21}H_{17}NO_4S$: C, 66.47; H, 4.52%. (The solution of the starting sulphone in ethanolic sodium ethoxide was filtered to remove traces of dinitrodifluorenylidenes.)

9-Methyl-9-fluorenyl phenyl sulphone (76%) crystallized as plates from ethanol, m.p. 164–166°, identical with the sample described above.

Methyl 9-methyl-9-fluorenyl sulphone (69%) formed colorless prisms from hexane, m.p. 134–136°, identical with the sample described above.

Methyl 9-isopropyl-9-fluorenyl sulphone (72%) crystallized as almost colorless prisms from hexane, m.p. 122–124°. Found: C, 71.24; H, 6.10%. Calc. for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.33%.

Dimethyl 9,9′-Difluorenyl-9,9′-dicarboxylate

Methyl fluorene-9-carboxylate (2.3 g) was dissolved in methanol (50 ml) containing sodium methoxide (from sodium, 0.5 g). Addition of *p*-toluenesulphonyl chloride (3.5 g) resulted in the rapid separation of a microcrystalline solid. Recrystallization from chloroform–hexane gave small needles (1.7 g), m.p. 240–242°, identical with an authentic specimen of the above-named ester (10, 17). Found: C, 79.92; H, 4.81%. Calc. for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97%.

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