

ADDITION OF  $\alpha$ -HALOSULFINYL CARBANIONS TO IMINES.  
 CONVENIENT PREPARATIONS OF SUBSTITUTED AZIRIDINES AND PYRROLES

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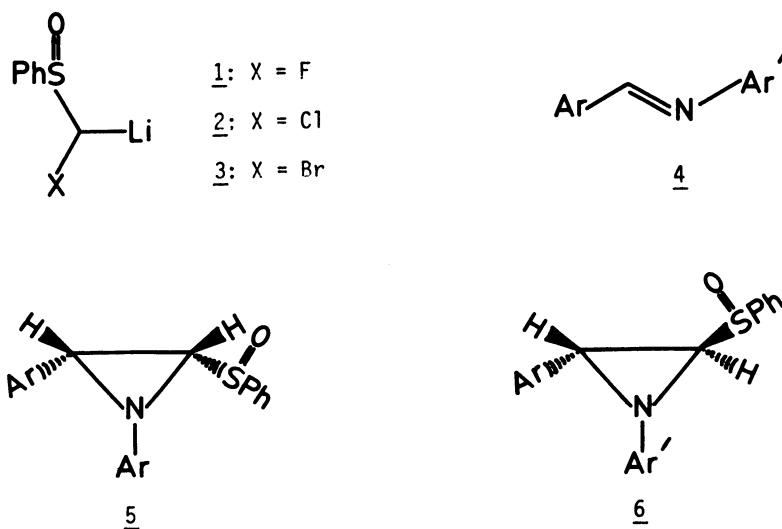
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$\alpha$ -Lithio- $\alpha$ -chloro- and - $\alpha$ -fluoromethyl phenyl sulfoxides react with N-(benzylidene)anilines to give the corresponding aziridines in good yields. Pyrolyses of these compounds in the presence of dimethyl acetylenedicarboxylate result in substituted pyrroles in high yields.

Recent work from our laboratory has demonstrated applications of  $\alpha$ -lithio- $\alpha$ -halomethyl phenyl sulfoxides in the syntheses of  $\alpha\beta$ -unsaturated carbonyl compounds, halomethyl ketones, vinyl halides and vinyl sulfides.<sup>1)</sup> It is noteworthy that of the three  $\alpha$ -lithio- $\alpha$ -halomethyl phenyl sulfoxides (1, 2, and 3) studied, the  $\alpha$ -fluoromethyl derivative 1 seems to be the most stable one. This observation could be explained on the basis of the inductive effect of the  $\alpha$ -halogen atoms.<sup>2)</sup> This communication reports the comparative studies on the reaction of N-(benzylidene)anilines with the carbanions 1 and 2.<sup>3)</sup> The process provides a very convenient route to phenylsulfinylaziridines.<sup>4)</sup>



The reaction of carbanion 1 with the imines 4 led to higher yields of 5 and 6 than those obtained from the reaction of 2 and 4 (except when Ar = p-nitrophenyl-). This is probably due to the greater stability of the anion 1 which is also less sterically crowded than 2. The results are summarized in Table 1.

Table 1.

Ar	<u>4</u>	Ar'	<u>5</u> + <u>6</u> / % <sup>a)</sup> From <u>4</u> with <u>1</u>	<u>5</u> + <u>6</u> / % <sup>a)</sup> From <u>4</u> with <u>2</u>	Ratio <sup>b)</sup> <u>5</u> : <u>6</u>
C <sub>6</sub> H <sub>5</sub> -		C <sub>6</sub> H <sub>5</sub> -	75	63	1:1.6
p-ClC <sub>6</sub> H <sub>4</sub> -		C <sub>6</sub> H <sub>5</sub> -	100	96	1:1.2
p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -		C <sub>6</sub> H <sub>5</sub> -	42	60	-c)
C <sub>6</sub> H <sub>5</sub> -		p-BrC <sub>6</sub> H <sub>4</sub> -	98	96	1:2.4
C <sub>6</sub> H <sub>5</sub> -		p-MeC <sub>6</sub> H <sub>4</sub> -	100	82	1:1.9

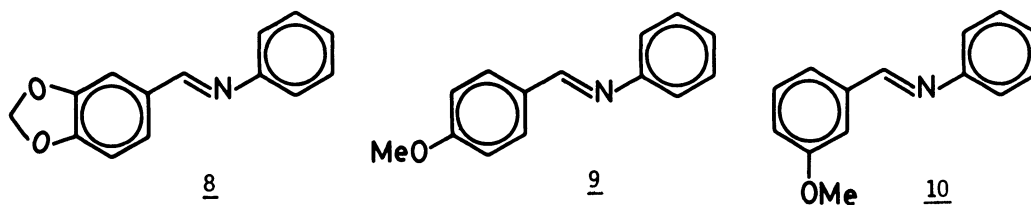
<u>7</u> , 40%	<u>7</u> , 33%	-d)

a) Products were purified by PLC-chloroform. b) Determined by NMR. Values given derived from the reaction of 4 and 2. The reaction of 4 with 1 gave similar ratio. c) Only the *cis* isomer was obtained. d) Only the *trans* isomer was isolated.

The following procedure is representative:  $\alpha$ -lithio- $\alpha$ -fluoro- or - $\alpha$ -chloro-methyl phenyl sulfoxide was generated by the reaction with lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at  $-78^\circ\text{C}$ .<sup>1)</sup> N-(benzylidene)anilines were added at this temperature and the reaction mixtures were stirred overnight at room temperature. The reactions were quenched with saturated aqueous ammonium chloride. The crude product was isolated with chloroform and further purified by preparative layer chromatography (PLC). Recrystallization from ether-hexane gave the *trans* isomer as a solid. The *cis* isomer was isolated from the mother liquor as an oil slightly, contaminated with the *trans* isomer.

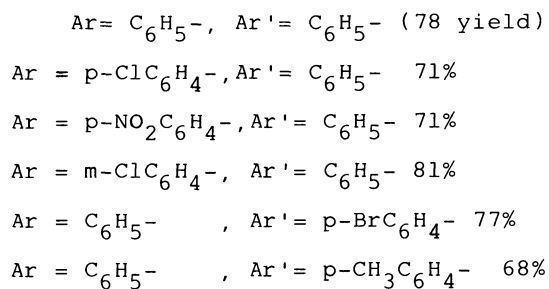
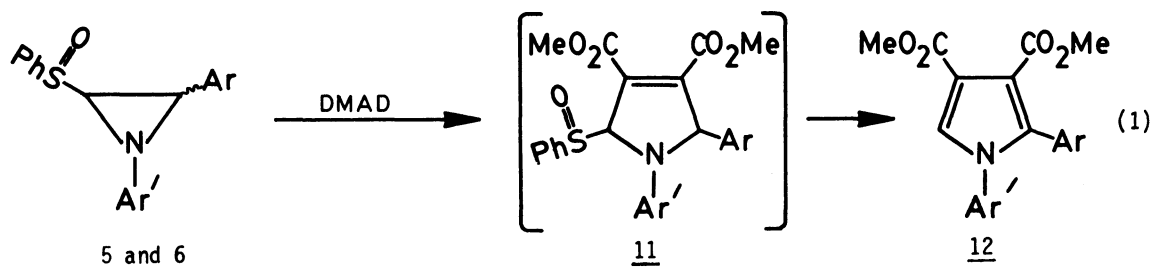
The stereochemistry of the *cis*- (5) and the *trans*-aziridines (6) were determined on the basis of the coupling constants of the two aziridine hydrogens. The coupling constants of hydrogens in 5 and 6 were 6.0 and 2.0-2.5 Hz respectively. These values agreed well with those reported for the *cis*- and the *trans*-aziridines.<sup>5)</sup> The coupling constant of the two hydrogens of compound 7 was 2 Hz.<sup>4)</sup>

N-(benzylidene)anilines with the para electron donating and activating substituents on the aromatic ring, e.g. imines 8 and 9, failed to react with both carbanions 1 and 2 due to the increase in electron density at the imine carbon.



The addition of carbanion 2 to imine 10 gave the expected aziridine in 79% yield.

Pyrolysis of the aziridines (a mixture of *cis* and *trans* isomers) in a sealed tube in toluene and dimethyl acetylenedicarboxylate (DMAD) at 90 °C for 6 h gave the pyrroles directly in high yields. Presumably, the reaction involved the addition of azomethine ylides,<sup>6)</sup> derived from the thermal ring opening of aziridines, to DMAD followed by the elimination of the benzene-sulfinic acid from the intermediate pyrrolines 12.<sup>7)</sup> The process represents a convenient one-step synthesis of substituted pyrroles 12 from aziridines.<sup>7)</sup> The reaction of 7 with DMAD gave a complex mixture and no pyrrole could be isolated. The results are summarized in Eq.1.



Our results represent a novel synthetic application of the carbanions from  $\alpha$ -halomethyl phenyl sulfoxide. It demonstrates that the  $\alpha$ -halomethyl phenyl sulfoxide could function as the species 13. It also provides a convenient procedure for the synthesis of substituted aziridines and pyrroles.



#### References

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