

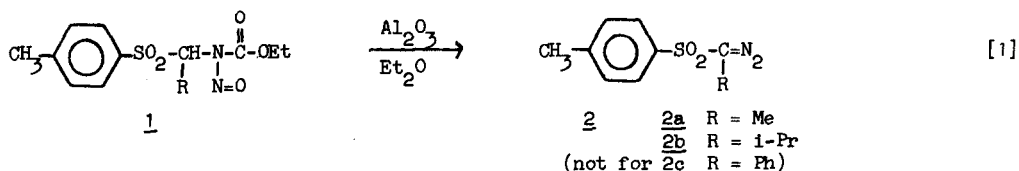
ON THE SYNTHESIS OF  $\alpha$ -PHENYLTOSYLDIAZOMETHANE<sup>1</sup>

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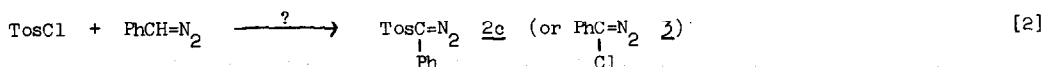
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A recent preliminary paper by Dahn and coworkers<sup>2</sup> is devoted to the problem of the synthesis of  $\alpha$ -substituted tosyldiazomethanes 2a-c. For various reasons their communication is of interest. The results of Dahn agree very much with our earlier observations<sup>3</sup> as far as  $\alpha$ -diazosulfones are concerned with aliphatic substituents, like 2a and 2b. However, our mutual experiences with  $\alpha$ -phenyltosyldiazomethane (2c) are quite conflicting.

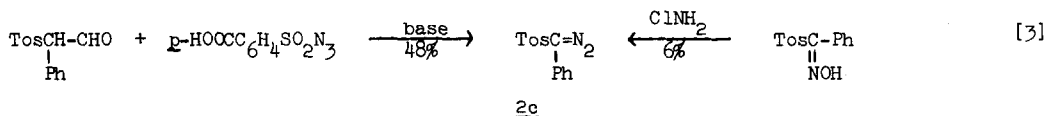


In our laboratory, *n*-alkyl substituted  $\alpha$ -diazosulfones<sup>4</sup>, including 2a<sup>5</sup> (*i.e.* R = Me) and 2 (R = Et) have been prepared previously by the alumina-induced cleavage of the *N*-nitrosocarbamates given in eq. [1]<sup>3</sup>, a method introduced originally for the synthesis of sulfonyldiazomethanes 2 (R = H).<sup>6</sup> With increasing size of the group R, however, the synthesis of the precursory *N*-nitrosocarbamates becomes progressively more difficult. We have been unable to isolate *N*-nitrosocarbamate 1b (*i.e.* R = 1-Pr) by nitrosation of the corresponding carbamate with nitrosyl chloride in pyridine.<sup>3</sup> It now appears that Dahn and his group did succeed after all, and also that they were able to convert 1b (without being isolated) into  $\alpha$ -diazosulfone 2b, according to eq. [1].<sup>2</sup> Neither group, apparently, has succeeded in the synthesis of 1 (R = Ph), and consequently  $\alpha$ -phenyltosyldiazomethane (2c) cannot be prepared by reaction [1].<sup>3,2</sup>

According to Dahn,  $\alpha$ -phenyltosyldiazomethane (2c) is formed, however, in solution by reaction [2], but the compound is reported to be too unstable to allow for "isolation and further structural investigation".<sup>2</sup> We find these assertions incompatible with reality.



We have prepared  $\alpha$ -phenyltosyldiazomethane (2c) (and analogues) by two independent routes<sup>1</sup>: by application of the diazo-transfer reaction<sup>7</sup> and of the Forster reaction<sup>8</sup>, as indicated in eq. [3]. In our hands 2c is a red, crystalline solid — that perfectly well can be isolated and characterized — melting under decomposition at 79-81° (Kofler block); IR (nujol) 2085 ( $\nu_{\text{C=N=N}}$ ), 1342 and 1152  $\text{cm}^{-1}$  ( $\text{SO}_2$ ); NMR ( $\text{CCl}_4$ )  $\delta$  2.38 (s, 3 H), 7.05-7.35 (m, 7 H), 7.67 (d, 2 H,  $J = 8.5$  Hz); correct elemental analysis. With hydrochloric acid in ether, 2c is converted quantitatively to  $\alpha$ -chlorobenzyl *p*-tolyl sulfone.



Furthermore, we feel it highly unlikely that 2c can be prepared by reaction [2]. It is known that diazomethane itself cannot be sulfonylated by sulfonyl chlorides.<sup>9</sup> It is also known that the reaction of carbon nucleophiles with sulfonyl chlorides usually leads to chlorination rather than sulfonylation.<sup>10</sup> Therefore chances are that the unstable diazo compound observed by Dahn in fact has been  $\alpha$ -chlorophenyldiazomethane (3), an unknown compound that may very well be unstable indeed.

Finally,  $\alpha$ -diazobenzyl 1,2-diphenylvinyl sulfone, m.p. 112-114° (dec.), reported by Carpino et al.<sup>11</sup>, should be mentioned as the first representative of the sulfonylphenyldiazomethanes.

#### Notes and References

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3. a. A.M. van Leusen and J. Strating, Quart.Rep.Sulfur Chem. **5**, 67 (1970); b. A.M. van Leusen, thesis, Groningen University, 1965.
4. In addition to the compounds mentioned in this paper, special types of  $\alpha$ -alkyl- $\alpha$ -diazosulfones were obtained by addition of tosyldiazomethane (2, R = H) to enamines, A.M. van Leusen, B.A. Reith, R.J. Mulder and J. Strating, Angew.Chem. **83**, 290, or Intern.Ed. **4**, 271 (1971), and to aldehydes, A.M. van Leusen and Daan van Leusen, unpublished results.
5. The physical data reported by Dahn et al.<sup>2</sup> for 2a and its precursor 1a are in good agreement with our observations, except for some (probably insignificant differences) in the decomposition temperatures. We found ca. 40° (lit.<sup>2</sup> 52-55°, dec.) and 95° (lit.<sup>2</sup> 77-79°) for 2a and 1a, respectively; and for the phosphazine derivative of 2a ca. 145° (lit.<sup>2</sup> 162-164°).
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