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SYNTHESIS OF UNSYMMETRICAL BENZYLIC SULFOXIDES

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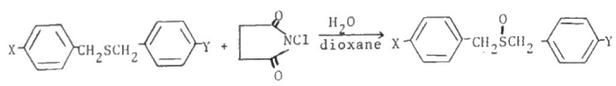
ABSTRACT

Six unsymmetrical benzylic sulfides have been oxidized to the corresponding sulfoxides by N-chloro-succinimide in 90% aqueous dioxane solution. Physical constants and combustion analysis data for these new compounds are provided. The compounds prepared, $XC_6H_4CH_2S(O)CH_2C_6H_4Y$, where X and Y are **para** substituents are:**1b,** X= Cl, Y= NO_2; **2b,** X=Cl, Y= CN; **3b,** X=Cl, Y=CH_3; **4b,** X=Cl, Y=H; **5b,** X=OCH_3, Y=H; **6b,** X=CH_3, Y=H.

Many positive halogen compounds have been recently employed for the oxidation of sulfides to sulfoxides[1-3]. One interesting procedure for this type of transformation which has been reported involves the use of N-bromosuccinimide in aqueous solvents at room temperature.[4] This method is rather limited in scope, as aliphatic sulfides appear to undergo C-S bond cleavage under the reaction conditions.[4]

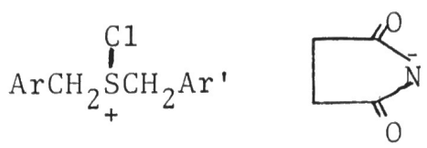
We have found that unsymmetrical benzylic sulfides **1a-6a** are oxidized to the corresponding sulfoxides **1b-6b** by N-chlorosuccinimide in aqeous dioxane solution. The results are summarized in Table I (the percent yields reported in the table are based on purified products). Infrared spectra of the sulfoxides exhibited strong absorpation at 1030-1040 cm.$^{-1}$, characteristic of the S-O moiety. The simplicity of this method, coupled with the low cost and stability of the oxidizing agent indicate its usefulness for the preparation of benzylic sulfoxides.

Table I



	1a-6a		1b-6b
Compound	X	Y	Yield (%)
1b	Cl	NO_2	81
2b	Cl	CN	77
3b	Cl	CH_3	81
4b	Cl	H	81
5b	OCH_3	H	70
6b	CH_3	H	78

Benzylic sulfides are converted by N-chloro-succinimide in non-aqueous media to *alpha*-chloro sulfides.[5] The mechanism of this transformation is believed to involve the intermediacy of chlorosulfonium salts, such as **7**. Hydrolysis of chlorosulfonium salt **7** would logically produce the sulfoxide product observed in aqueous dioxane solution.



7

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EXPERIMENTAL

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained using a Beckman IR-10 spectrophotometer. N-Chlorosuccinimide was purified by rapid recrystallization from eight times its weight of water. Preparation of sulfides **1a-6a** has been previously described.[5]

GENERAL PROCEDURE FOR OXIDATION. To a solution of 5.0 g. of the sulfide dissolved in 50 ml. of 90% aqueous dioxane at room temperature was added rapidly, with stirring, an equimolar amount of N-chloro-succinimide. The resultant solution was allowed to stir for an additional hour, and was then diluted with approximately 400 ml. of water. The crude sulfoxide was isolated by filtration and was purified by recrystallization. Pertinent data for sulfoxides **1b-6b** are summarized in Table II.

TABLE II

Compound		m.p. (°C)	Rec'n Solvent	Calc'd %C	Calc'd %H	Found %C	Found %H
1b	($C_{14}H_{12}C1NO_3S$)	144-145	ethanol-water	54.28	3.90	54.04	4.14
2b	($C_{15}H_{12}C1NOS$)	143-144	methanol-water	62.17	4.18	61.92	4.23
3b	($C_{15}H_{15}C1OS$)	151-152	methanol-water	64.62	5.42	64.41	5.54
4b	($C_{14}H_{15}C1OS$)	129-130	benzene-hexane	63.51	4.95	63.11	4.98
5b	($C_{15}H_{16}O_2S$)	128-129	methanol-water	69.20	6.19	69.23	6.22
6b	($C_{15}H_{16}O_2S$)	100-101	benzene-hexane	73.73	6.60	73.82	6.54

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