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EFFECTS OF SOLVENTS ON THE REACTION OF 2,2-DIMETHYLPROPANESULFINYL CHLORIDE WITH ACTIVATED ZINC

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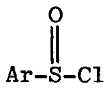
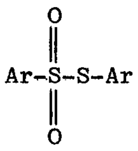
Abstract: Although 2,2-dimethylpropanesulfinyl chloride reacts with zinc in C_6H_6 or CCl_4 to give the corresponding thiosulfonate as major product, the reaction in $C_2D_{10}O$, $C_2H_{10}O$, and CD_3CN affords the corresponding thiosulfinate as the major product.

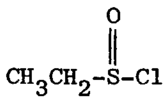
Several aromatic sulfinyl chlorides (1) react with Cu in CCl_4,[1,2] with Ag in petroleum ether (bp 60°-80°),[3,4] or with Zn in ether[5-7] to give the corresponding thiosulfonate 2. The reaction of ethanesulfinyl chloride (3) with Zn in ether gives S-ethyl thioethanesulfonate (4).[5] During the course of studying the chemistry of α-disulfoxides (5),[8-10] several interesting solvent effects


$\mathrm{Ar{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}Cl}$

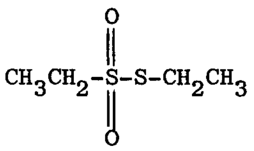
1


$\mathrm{Ar{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}{-}S{-}Ar}$

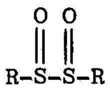
2


$\mathrm{CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}Cl}$

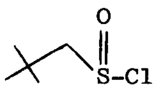
3


$\mathrm{CH_3CH_2{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}{-}S{-}CH_2CH_3}$

4


$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}R}$

5



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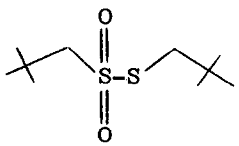

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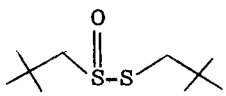
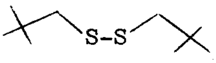


8

were observed in the reaction of 2,2-dimethylpropanesulfinyl chloride (6) with Zn.

When 6 is stirred with activated Zn[11] in CCl_4 at 25° for 24 h the only product observed by TLC, IR, and ^1H NMR is S-2,2-dimethylpropyl thio-2,2-dimethylpropanesulfonate (7). Compound 7 was isolated in 78% yield. Similarly, stirring 6 with Zn in benzene at 6° for 1.5 h gives a 79% yield of 7 (NMR assay, 40% of 6 recovered).

When the reaction of 6 with Zn was carried out in ether-$\underline{d}_{10}$ at 0° for 1 h and then filtered, ^1H NMR and ^{13}C NMR showed the presence of S-2,2-dimethylpropyl thio-2,2-dimethylpropanesulfinate (8, 50%), 2,2-dimethylpropyl disulfide (9, 5%), and zinc 2,2-dimethylpropanesulfinate (10, 44%). Compound 10 slowly precipitated from the reaction mixture. Acidification at 0° with 60% H_2SO_4 followed by ether extraction converted 10 to the free acid (2,2-dimethylpropanesulfinic acid, 11) which was identified by ^1H NMR and IR.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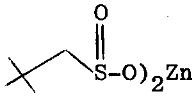
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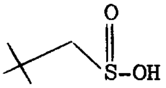
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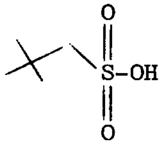
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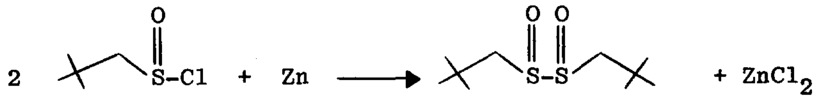
The above reaction was also carried out in ether and the reaction mixture after 1 h at 0° was stirred with saturated NH_4Cl. The layers were separated and the ether layer was evaporated at 0°. TLC, ^1H NMR, ^{13}C NMR, and IR analysis showed that the ether layer residue contained 7 (13%) and 8 (80%). The ^{13}C NMR spectrum contained an additional resonance at δ 62.46 that can be assigned to 2,2-dimethylpropanesulfonic acid 12.[13]

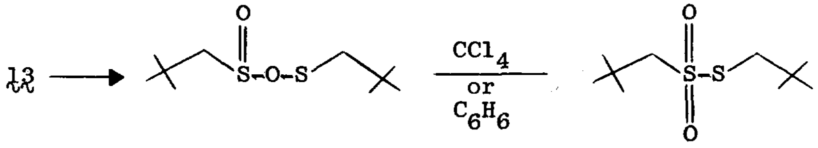
The reaction of 6 with Zn at 0° in acetonitrile-$\underline{d}_3$ for 1 h, followed by filtration, gave the following distribution of products: 7 (18%), 8 (53%), 9 (13%), and 10 (18%) (NMR assay).

The above results show that CCl_4 and C_6H_6 are the solvents of choice for converting 6 to 7 and that ether and acetonitrile are useful for preparing 8 and 10.

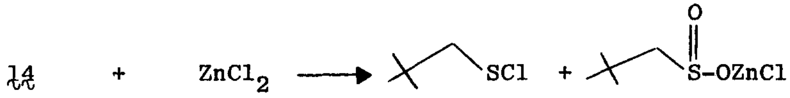
The distribution of products mentioned above is similar to the distribution of products obtained from the oxidation of 8[8] and suggests a common intermediate, namely α-disulfoxide 13. The formation of products other than 7 in ether and acetonitrile-$\underline{d}_3$, where $ZnCl_2$ is soluble, suggests that $ZnCl_2$ reacts with 13 to give 8 and 10, possibly via sulfenyl sulfinate 14, 2,2-dimethylpropanesulfenyl chloride (15), and chlorozinc salt 16, as shown below.



6 13 (1)



14 7 (2)

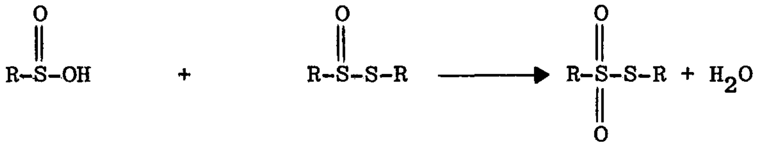


15 16 (3)

$$14 + 15 \longrightarrow 6 + 8 \qquad (4)$$

$$14 + 16 \longrightarrow 10 + 15 \qquad (5)$$

Although alkanesulfinic acids (17) generally react rapidly with thiosulfinates (18) to give thiosulfonates (19),[15,16] 11 appears to be unreactive toward 8,[8,16] possibly due to steric hindrance (eq 6). Therefore, the formation of 4 in the reaction of 3 with Zn in ether probably results from the reaction of ethanesulfinic acid, which is in equilibrium with the zinc salt in the presence of traces of water, with the corresponding thiosulfinate (eq 6).[15]



$$R\text{-}S(=O)\text{-}OH + R\text{-}S(=O)\text{-}S\text{-}R \longrightarrow R\text{-}S(=O)_2\text{-}S\text{-}R + H_2O \qquad (6)$$

17 18 19

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