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SYNTHESIS OF ALKENESULFONIC ACIDS AND CHLORIDES. *IN SITU* SULFONE CHLORINATION – RAMBERG-BÄCKLUND REACTIONS WITH CCl_4-KOH

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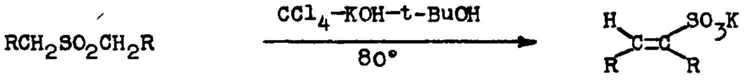
An extension of our studies[1] on reactions of α-sulfonyl carbanions with CCl_4 has revealed, unexpectedly, that di-primary alkyl sulfones (I) are transformed into cis-dialkylethenesulfonic acid salts (II; eq 1).[2]

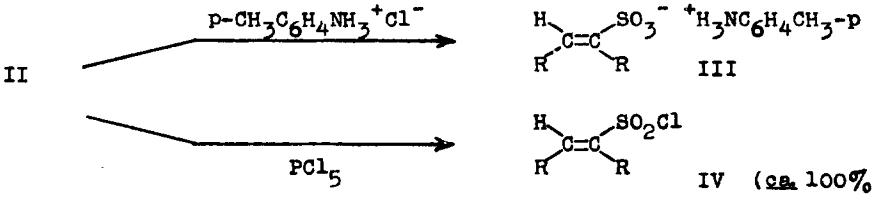


(1)

I R = alkyl II (>70%)

Little information is available on the chemistry of compounds II and their derivatives, ostensibly because they have not been generally accessible. Ethenesulfonic acid and its derivatives are reactive olefinic species;[3] the α,β-dialkyl homologs should exhibit related reactivity. The simple synthesis of II resulting from this study should now facilitate investigations of this class of compounds.

Compounds II were easily converted into crystalline p-toluidinium salts (III; eq 2) for elemental analysis, and into sulfonyl chlorides (IV; eq 3) for stereochemical structure determination[2] and projected synthetic work.



(2)

III

(3)

IV (ca. 100%)

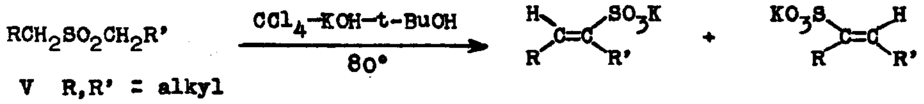
The following procedures are general, the specific data representing compounds I–IV in which both R's, respectively, are: a, Me; b, Et; c, n-Pr; and d, n-heptyl. These compounds have not been previously reported.

Preparation of II. For each 0.01 mol of I,[4] 4 g of powdered KOH, 10 ml of t-BuOH, and 10 ml of CCl_4 are added and the mixture is vigorously stirred under reflux (80°) for 5–10 hr, a few drops of H_2O being added after the first 2 hr. The mixture is concentrated to dryness (in vacuo) and the residue is washed with ether to remove any unchanged I. This residue is continuously extracted (Soxhlet) with hot t-BuOH; evaporation of the extract leaves II, generally a tan powder when dried. Alternatively, the reaction mixture is cooled (ice bath), neutralized to pH 7 with dil H_2SO_4 and concentrated to dryness. Trituration with ether removes any residual I. The solid mass is washed several times with hot EtOH; evaporation of the combined washings leaves II as an off-white dry powder.[5] Most of I is consumed within 5 hr; the yields are usually >70%. The ir spectrum (ν, cm^{-1}, Nujol) of each product exhibited strong bands near 1225, 1176 (or a broad band near 1190) and near 1050 for SO_3^-; and a medium band above 1600 for C=C. Nmr (τ, in D_2O, sodium 3-(trimethylsilyl)-1-propanesulfonate as internal standard) for HC=C of a, 3.63, quartet, 1 H; b, 3.66, triplet, 1 H; c, 3.40, triplet, 1 H; and d, 3.68, triplet, 1 H.

Preparation of III. Saturated aqueous solutions of II and of p-toluidine hydrochloride are combined. Crystalline III generally separates slowly, aided by chilling. Recrystallization (heptane-EtOH) provides white, sharp-melting crystals. Mp (cor) of a, 133–134°; b, 140–141°; c, 165–166°; d was an uncrystallizable oil. Elemental analysis[6] of each crystalline product was satisfactory for the structure assigned. The ir spectrum (ν, cm^{-1}, Nujol) of each product exhibited strong bands near 1190, 1165, and 1040 for SO_3^-; a weak band near 1630 for C=C; and a medium band near 2640 for NH_3^+. Nmr (τ, in DMSO-d_6, TMS as internal standard) for HC=C of a, 3.91, quartet, 1 H; b, 4.00, triplet, 1 H; c, 3.67, triplet, 1 H; and d, 3.87, triplet, 1 H.

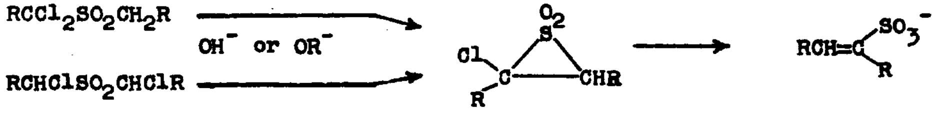
Preparation of IV.[7] A mixture of dry II with twice its weight of PCl_5 is suspended in $CHCl_3$ and vigorously stirred at 25-35° for 1-2 hr. The solids are removed and the filtrate is washed with aqueous $NaHCO_3$, dried over $MgSO_4$ and evaporated leaving a pungent pale-yellow oil. Yields are almost quantitative. Distillation under reduced pressure affords a colorless oil essentially identical to the undistilled product (ir, nmr). Bp of b, 65-67°/0.8 mm; c, 73-75°/0.4 mm; and d, 70-75°/0.2 mm. The ir spectrum (ν, cm^{-1}, neat and in CS_2) of each product exhibited bands near 1370 and 1180 for SO_2; and a medium band near 1640 for C=C. Nmr (τ, in CCl_4, TMS as internal standard) for HC=C of a, 3.14, quartet, 1 H; b, 3.26, triplet, 1 H; c, 3.22, triplet, 1 H; and d, 3.15, triplet, 1 H.

As indicated by the examples above, symmetrical sulfones are converted into alkenesulfonic acids with surprising isomer specificity. The physical constants, especially the nmr spectra, of II, III, and IV present clear evidence of the presence of a single isomer in each case. As might be expected, unsymmetrical sulfones (V) provide two positionally isomeric alkenesulfonic acids, both having the cis configuration (eq 4). For example, ethyl n-propyl sulfone was converted into a mixture of cis-2-pentene-2-sulfonic acid (53%) and cis-2-pentene-3-sulfonic acid (47%) as the potassium salts.



(4)

Based on the original work of Ramberg and Backlund with bis(α-bromoethyl) sulfone[8] more recent studies have shown that gem-α-dichloro sulfones as well as α,α'-dichloro sulfones are converted into alkenesulfonic acids in alkaline media, indicating the intermediacy of chloro episulfones (eq 5).[9] Our



(5)

initial studies[1] demonstrated that ketones and sulfones are readily α chlorinated by CCl_4-KOH. It is probable, therefore, that di-primary alkyl sulfones are first transformed into the *dichloro sulfones* under these conditions, thereby providing the alkenesulfonic acids (*cf.* eq 1 and 5).

However, these results were unexpected because benzyl sulfone (also a di-primary alkyl sulfone) and di-*sec*-alkyl sulfones are only *monochlorinated* under identical conditions, being almost quantitatively converted into the simple alkenes expected from Ramberg-Backlund reactions.[1] The mechanisms of the surprising transformations described here will be reported shortly.

NOTES AND REFERENCES

1. C. Y. Meyers, A. M. Malte, and W. S. Matthews, *J. Amer. Chem. Soc.*, **91**, 7510 (1969); C. Y. Meyers, A. M. Malte, and W. S. Matthews, *Quart. Rept. Sulfur Chem.*, **5**, 229 (1970).
2. Determination of the *cis* configuration of these products (*i.e.*, having only one olefinic hydrogen atom) required a special technique which is described by C. Y. Meyers and I Sataty, *Tetrahedron Letters*, this issue.
3. H. Distler, *Angew. Chem. Intern. Ed. Engl.* , **4**, 300 (1965).
4. These sulfones are simply prepared by oxidation of the sulfides obtained by the reaction of alkyl halides with Na_2S or of 1-alkenes with H_2S; See W. J. Hickinbottom, "Reactions of Organic Compounds," 3rd Ed., Longmans, Green and Co., London, 1957, pp 175 ff, 559 ff; and C. M. Suter, "The Organic Chemistry of Sulfur," Reprinted Ed., Intra-Science Research Foundation, Santa Monica, Calif., 1969, Chapter 7.
5. Aqueous solutions of II prepared by the first procedure may be slightly alkaline. The alternative procedure affords neutral solutions and is preferred, although it is somewhat more tedious.
6. Galbraith Laboratories, Knoxville, Tenn.
7. E. F. Landau, *J. Amer. Chem. Soc.*, **69**, 1219 (1947), prepared ethenesulfonyl chloride by a similar method.
8. L. Ramberg and B. Backlund, *Arkiv Kemi, Mineral., Geol.*, **13 A**, No. 27, (1940), footnote p. 17.
9. F. G. Bordwell and S. C. Crooks, *J. Amer. Chem. Soc.*, **91**, 2084 (1969), and earlier papers; L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, **90**, 6790 (1968), and earlier papers.