

Test.⁴ Treatment of I with acetic anhydride and sulfuric acid² yields scyllitol hexaacetate, m.p. 286°,⁵ in 60–70% yield (based on the cyclitol content of I). *Anal.* Calcd. for C₁₈H₂₄O₁₂: C 49.95, H 5.60. Found C 49.93, H 5.67. Myo-inositol hexaacetate was not detected as a product. After acidification of I with sulfuric acid, the resultant solution was subjected to repeated evaporation to dryness *in vacuo* at 50° with methanol. The final residue was taken up in water, deionized with Amberlite MB-3, and the eluate again taken to dryness *in vacuo*. The deionized residue, obtained in 90% yield from I (based on cyclitol content of I), was shown to give only one spot with the same *R_f* as scyllitol in paper chromatography with phenol-water or acetone water.

From microanalysis⁶ data, and with the assumption that it is monomolecular, compound I appears to be a monohydrate of scyllitol diborate. Calcd. for C₆H₈O₈B₂Na₂·9H₂O; C 16.45, H 5.99, B 4.94, water content 37.02. Found C 16.52, H 6.07, B 4.87. Weight loss on drying at 100° for 18 hr., 37.27.

If scyllitol is heated at 100° with 0.125*M* borate, a compound migrating at the same rate as I in borate ionophoresis is obtained. Presumably this is also scyllitol diborate. The stereochemistry of the borate complex is still unproved and is being further investigated.

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Received December 30, 1957

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(5) Melting point determined on a Fisher-Johns melting point block.

(6) I am indebted to Dr. W. C. Alford of the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health for the microanalyses.

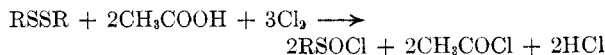
An Improved Method for Preparing Sulfinyl Chlorides

Sir:

The new method for the preparation of sulfinyl chlorides recently reported¹ represented a great improvement over previously available methods. The procedure has certain disadvantages, however, in that one has difficulty in determining when the stoichiometric quantity of chlorine has been added, a relatively large volume of inert solvent must be used to impart fluidity to the two-phase system, and the reaction must be carried out at

low temperatures to avoid the premature decomposition of the organosulfur trichloride.

We have recently found that if one mole of alkyl disulfide is mixed with exactly two moles of glacial acetic acid in the absence of solvent and chlorinated at 0° the reaction proceeds smoothly in a one-phase system and produces the desired sulfinyl chloride in high yield. On the first addition of chlorine the disulfide is transformed to the reddish orange sulfenyl chloride, RSCl. Additional chlorine apparently changes the sulfenyl chloride to the organosulfur trichloride, RSCl₃, which rapidly reacts with acetic acid to form acetyl chloride and the desired sulfinyl chloride. Since acetyl chloride is colorless and the sulfinyl chlorides are only faintly yellow, the disappearance of the reddish orange sulfenyl chloride color constitutes a good endpoint to indicate completion of the reaction. The products may be separated by fractionation of the reaction mixture without further treatment.



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Received January 6, 1958

Base-Catalyzed Rearrangement of α -Haloacetanilide into α -Anilinoacid Derivatives

Sir:

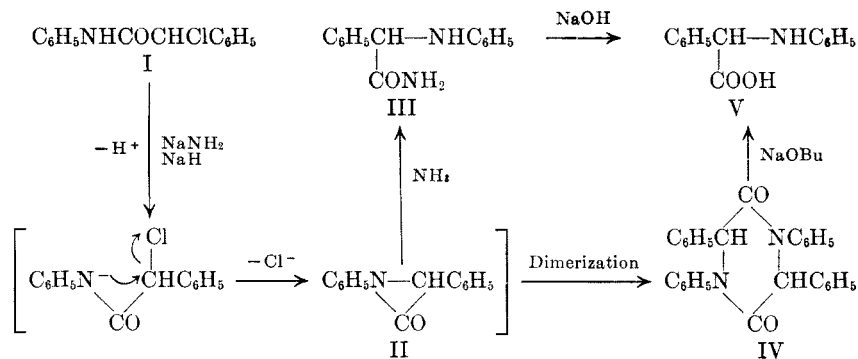
It has already been demonstrated that the action of sodamide in liquid ammonia upon β -chloropropionanilide and acrylanilide produces *N*-phenyl- β -lactam in fair yields.¹ In this communication we wish to report our results obtained in a study of the reaction of sodamide in liquid ammonia, and of a suspension of sodium hydride in dry benzene, upon α -chloro- α -phenylacetanilide (I). We have found that (I) gives by the action of sodamide in liquid ammonia a mixture of three compounds of which two have been identified as α -anilinophenylacetamide (III) and 2,5-diketo-1,3,4,6-tetrahydropiperazine (IV). Reaction of (I) with sodium hydride yielded IV as a major product.

To a solution of 5.1 g. (0.13 mole) of freshly prepared sodamide in 250 ml. of liquid ammonia was added 30 g. (0.12 mole) of solid (I)² with stirring during 1 hr. Within about 5 min. an orange-red solution was obtained which became brown-red at the end of the addition. The ammonia

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was allowed to evaporate overnight. The residue was extracted with dry ether leaving behind one gram (1%) of an insoluble yellow product, m.p. 260°. Repeated recrystallizations from glacial acetic acid yielded (IV), m.p. 277.5–278°, as a white crystalline product. *Anal.* Calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_2\text{N}_2$: C, 80.36; H, 5.30; N, 6.70. Found: C, 80.70; H, 5.5; N, 6.80. It gave a single band at 1667 cm^{-1} in the carbonyl region of the infrared spectrum. The ethereal extract was chromatographed over silica-gel whereupon (III) was obtained (37% yield) as colorless prisms (from benzene), m.p. 129.5–130.5°. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{14}\text{ON}_2$: C, 74.3; H, 6.2; N, 12.39. Found: C, 74.5; H, 6.4; N, 12.33. In the carbonyl region of the infrared spectrum (III) shows two absorption bands at 1680 cm^{-1} and 1700 cm^{-1} .

A suspension of (III) (1 g.) in 20 ml. of 1*N* sodium hydroxide was stirred and refluxed for 24 hr., at which time the solution became completely clear. An evolution of ammonia could be detected during the reflux period. From the cooled acidified solution crystalline α -anilinophenylacetic acid (V) (0.7 g., m.p. 174–175°) was recovered by ether extraction and crystallization from benzene. No depression in melting point was observed for a mixture with an authentic α -anilinophenylacetic acid (m.p. 174–175°) prepared from aniline and α -chlorophenylacetic acid, by the method of McKenzie and Bate.⁴ A mixture of (IV) (0.5 g.) and a solution of sodium (0.5 g.) in 10 ml. 1-butanol was refluxed for 8 hr. After addition of 1 ml. water the reflux was continued for another 30 min. From the acidified solution crystalline (V) (0.3 g., m.p. 174°⁴) was obtained after recrystallization from benzene. It was identical with an authentic specimen, as described above.

To a suspension of 0.3 g. sodium hydride in boiling benzene was added dropwise with shaking a solution of (I) (2.5 g., 0.01 mole) in 50 ml. dry benzene, during 30 min. in an atmosphere of nitrogen. A vigorous evolution of hydrogen was observed during addition. The mixture was stirred

for 18 hr. After filtration and removal of solvent at reduced pressure, the residue was extracted with dry ether, leaving behind 1.4 g. of insoluble white product, m.p. 277–278° (from glacial acetic acid), which was identified as (IV). From the ether extract 0.3 g. of a light yellow solid product was isolated, m.p. 79–81° (VI). *Anal.* Calcd. for $\text{C}_{14}\text{H}_{11}\text{CN}$: N, 6.70; mol. wt. 209. Found: N, 6.78; mol. wt. 220 (Rast). The structure of (VI) is currently under investigation.

The formation of (III) from (I) by the action of sodamide in liquid ammonia seems to be parallel to that of α -haloketones with strong bases.⁵ In a like fashion it is plausible to assume that (I) is converted by the action of bases first to a three-membered ring intermediate (II)⁶ (azacyclopropanone or α -lactam), which has so far not been isolated. This intermediate (II), presumably highly reactive, could be transformed to stable compounds either by dimerization into a six-membered ring product (IV)⁷ or by reacting with the solvent⁸ (ammonia) yielding an open-chain rearranged product (III). In an inert solvent only the first mechanism could operate, thus leading to a six-membered ring compound as the major product. This has been actually found in case of reaction of (I) with sodium hydride in benzene as solvent. Full account of this study will be published soon.

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Received December 2, 1957

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