

SYNTHESIS AND CHARACTERIZATION OF 2,6-DIMETHYL-
THIOPHENOL

Harold Kwart and Marshall Cohen

Contribution from the Department of Chemistry, University
of Delaware,
Delaware 19711, U.S.A.

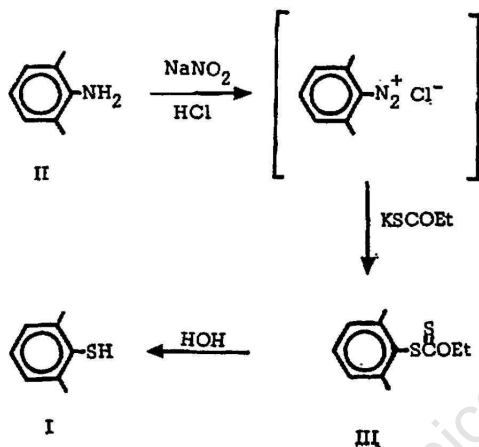
Recibido, noviembre 24 de 1967

RESUMEN

Se ha encontrado un nuevo método para la preparación de tioalcoholes aromáticos a partir de los fenoles correspondientes, formando primero el tion carbonato, que se convierte por calentamiento al tiol carbonato y del cual, por hidrólisis se obtiene el tioalcohol aromático. Este método se ha utilizado para preparar en grandes cantidades al 2,6 dimetil tiofenol. Se comprobó la alta pureza del compuesto y su identificación por medio de (cfv), IR y rmn.

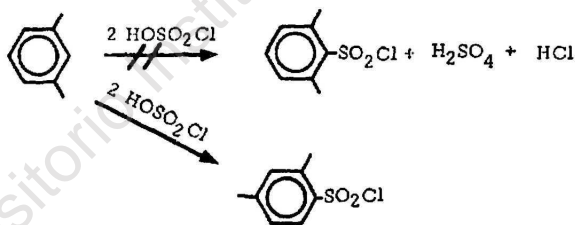
During the course of another study in progress in these laboratories it was necessary to secure a large amount of 2,6-dimethylthiophenol (I). The synthesis of this substance has been described only once previously (1) utilizing as starting material the difficultly available 2,6-dimethylaniline (II). In this procedure (Scheme I), II is converted to the diazonium chloride and the latter reacted with potassium ethyl xanthate affording a 33% yield of the dithiocarbonate (III). The desired product (I) is obtained on hydrolysis of III under vigorous conditions.

The usual procedure for preparing arenethiols from the corres-



Scheme 1

ponding sulfonyl chloride by reduction is not applicable here. The required sulfonylchloride has not been described before and cannot be formed as other arenesulfonyl chlorides *via* the chlorosulfonation of meta xylene; apparently because of steric hindrance in the familiar reaction expressed by Scheme 2, only the 2,4-dimethylbenzene sulfonyl chloride is formed.

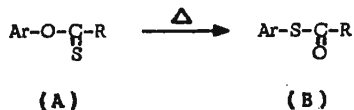


Scheme 2

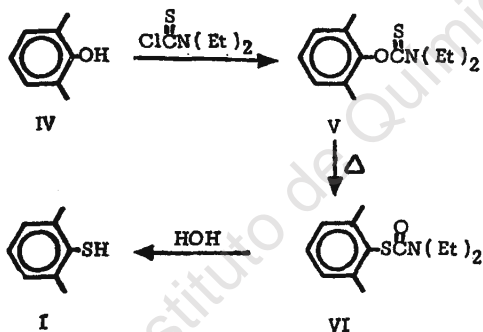
Recently a new approach (2,3) to the synthesis of arenethiols based on the Schönberg rearrangement (2) has been described. This method requires the corresponding phenol as starting material, which is then converted to a suitable thioncarbonate or thioncarbamate Ar O-C-R by reaction with the appropriate R-C-Cl reagent. This



sustance (A) rapidly undergoes thermal rearrangement to yield the thiolcarbonate or thiolcarbamate (B), from which ArSH can be readily isolated on hydrolysis.



Since both 2,6-dimethylphenol (IV) and N,N-diethylthiocarbonyl chloride are easily obtained commercially, this procedure offered a straightforward route to I according to the scheme 3.



Scheme 3

Step 1 was carried out using pyridine as the medium and gave a fair yield (ca. 51%) of V. The step 2, thermolysis, was performed as a vapor phase reaction according to the procedure of Kwart and Evans (2) and resulted in a high yield of product VI (even after careful distillation of the high boiling liquid). Infrared monitoring of the loss of the thiocarbonyl band and appearance of the carbonyl band constituted a very simple way of adjusting conditions of temperature and flow rate in Step 2 for purposes of attaining this yield.

The hydrolysis of VI to I gave some difficulties attributable to steric hindrance to hydrolysis of this 2,6-dimethyl "ester" substrate. The usual conditions (2,3) employing alcoholic KOH as a hydrolysis medium failed to effect reaction. However, using ethylene glycol - KOH and higher temperatures, while distilling off the diethyla-

mine, resulted ultimately in the pure thiol, where all other conditions tried did not succeed.

The structure and purity of I was confirmed by NMR and IR data which are given in the accompanying figures.

EXPERIMENTAL

2,6-Dimethylphenyl-N,N-diethylthiocarbamate (V).

In a 3-neck 3-liter flask equipped with an overhead stirrer, reflux condenser and N_2 inlet, was placed a solution of 200 g (1.64 moles) of 2,6-dimethylphenol and 163 g (1.07 moles) of *N,N*-diethylthiocarbamyl chloride (Pennsalt Chem. Corp.) in 1500 ml of dry pyridine. This mixture was refluxed for 5 hours with stirring under nitrogen.

The reaction solution was allowed to cool and then diluted with two liters of ether. This solution was washed with a total of 3.1 of 6M HCl in order to remove the pyridine; the acid was added with stirring and cooling. It was then washed with 1 l of water in small portions in order to remove pyridine hydrochloride.

The ether extracts were dried with anhydrous $MgSO_4$, and stripped under vacuum. The resultant liquid was vacuum distilled to give 130 g (51.4%) of the desired compound, a liquid - b.p. $185^\circ/1mm$ - which crystallized slowly on standing - m.p. $45-47^\circ$; IR (Fig. 1).

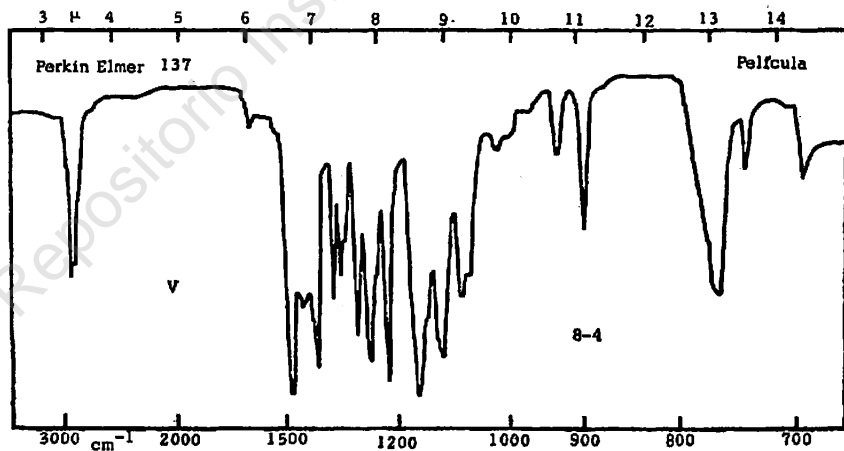


Fig. 1

Rearrangement of 2,6-dimethylphenyl-N,N-diethylthiocarbamate (V) to 2,6-dimethylphenyl-N,N-diethylthiolcarbamate (VI).

A solution consisting of 130 g of 2,6-dimethyl-N,N-diethylthioncarbamate (V) in 500 ml of dry toluene was passed slowly (by means of an infusion pump at a rate of about 50 ml/hr) through a vertical tube (internal diameter, 1 inch) heated to 400° by a regulated split furnace. The tube was continuously swept with a slow stream of dry nitrogen. The vapors were condensed at the bottom of the tube by an attached water cooled condenser.

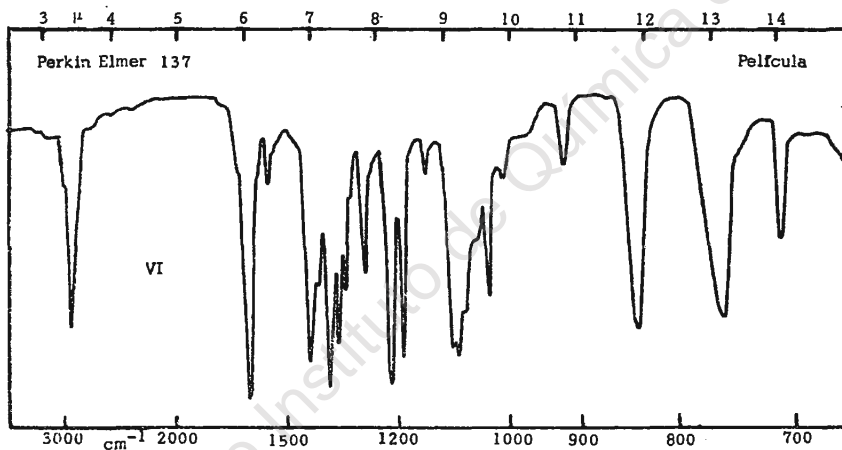


Fig. 2

After pyrolysis as described above, the toluene was removed under vacuum and the residual liquid vacuum distilled to give 114 g (87.6%) of the desired compound - b.p. 195/0.9mm. The IR spectra showed the disappearance of the thiocarbonyl band at 1520 cm^{-1} and the appearance of a carbonyl band at 1675 cm^{-1} (Fig. 2).

Hydrolysis of 2,6-dimethylphenyl-N,N-diethylthiolcarbamate (VI) to 2,6-dimethylthiophenol (I).

A 3-neck 3-liter flask was equipped with pot thermometer, overhead stirrer and a distillation take off. A solution of 350 g of KOH

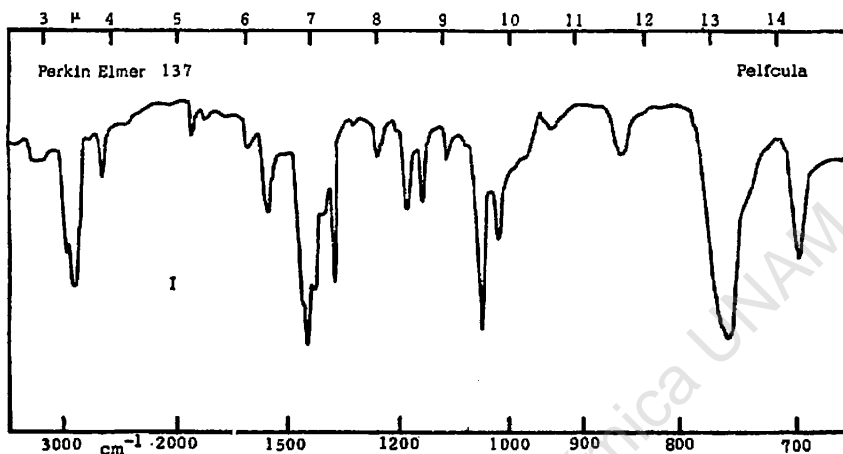


Fig. 3

pellets (6.25 moles) dissolved in 1 l of ethylene glycol was prepared in this flask with stirring and warming. With the aid of a dropping funnel 325 g (1.32 moles) of 2,6-dimethylphenyl-*N,N*-diethylthiocarbamate (VI) was then added and the flask heated up gradually to a pot temperature of 150°. At this pot temperature a mixture of diethyl amine and ethylene glycol was distilled off at a still head

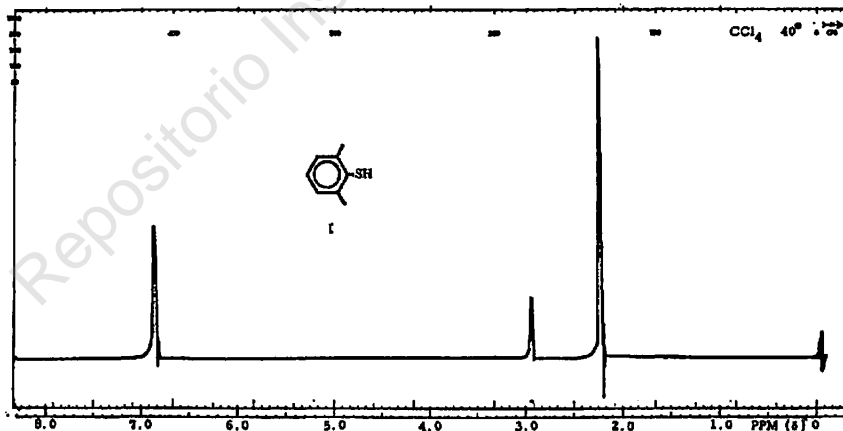


Fig. 4

temperature of 90°. The reaction was held at a pot temperature of 150° for 16 hrs. Finely divided K_2CO_3 precipitated from solution.

The reaction mixture was then cooled and transferred to a 5 l round bottom flask. A large quantity of water (1.5 l) was added with stirring, followed by 1 l of 9N H_2SO_4 . The acid was added with stirring and slowly, particularly in the beginning, to avoid excessive effervescence of CO_2 . After addition of all of the acid (making sure that the aqueous mixture was acid to litmus) the aqueous mixture was extracted continuously with pentane for 48 hrs.

The pentane solution was dried with anhydrous $MgSO_4$. After filtering off the drying agent and stripping the pentane, the remaining liquid was vacuum distilled to give 155 g (82%) of the desired 2,6-dimethylthiophenol - b.p. 45/1mm as confirmed by its IR and NMR spectra (Fig. 3 and 4).

Anal. Calcd. for $C_8H_{10}S$, C, 69.50; H, 7.29; S, 23.19. Found, C, 69.39; H, 7.37; S, 23.06.

ABSTRACT

A new method (2,3) for the synthesis of arenethiols from the corresponding phenols *via* thermal rearrangement of the thioncarbamate to the thiolcarbamate has been applied for the preparation of 2,6-dimethylthiophenol in pure form and in large quantities. The product purity and identification has been confirmed by (vpc), IR and NMR data which are provided in full detail.

REFERENCES

1. H. C. Godt, Jr. and R. E. Wann *J. Org. Chem.*, **26**, 4047 (1961).
2. H. Kwart and E. R. Evans, *ibid.*, **31**, 410 (1966).
3. M. S. Newman and H. A. Karnes, *ibid.*, **31**, 3980 (1966).