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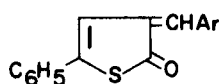
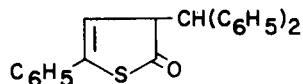
A New Method of Preparation and Some Reactions of γ -Thiolactones

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Detailed studies of the infrared and nuclear magnetic resonance spectra of 5-oxo-2-thiolenes derivatives have been reported recently by Gronowitz and co-workers (1, 2, 3). These γ -thiolactones have been prepared previously in low yield by heating γ -ketoacids with phosphorus pentasulfide in pyridine (4, 5).

As part of our study of the behavior of thiolacetic acid with γ -lactones (6), we have found that $\Delta^{\beta,\gamma}$ -butenolides react smoothly with thiolacetic acid to give the corresponding Δ^2 -thiolenes-5-ones in generally good yields. Thus, α -benzylidene- γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide (7) gave Ia in 56% yield. Similarly, γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide and α -angelica lactone (the γ -methyl analog) were also converted to the corresponding thiolactones. The advantage of this method is the ready availability of the butenolides (8).

Compound Ia reacts with phenylmagnesium bromide and with benzene under Friedel-Crafts conditions to give 4-benzhydryl-2-phenyl- Δ^2 -thiolenes-5-one (II) by 1,4-addition to the *cis* α,β -unsaturated carbonyl system. The structure of II was confirmed by analytical data, its infrared spectrum, and by comparison with a sample prepared from γ -phenyl- α -benzhydryl- $\Delta^{\beta,\gamma}$ -butenolide (9) and thiolacetic acid. The carbonyl absorption at 1705 cm^{-1} is in the region characteristic of γ -thiolactones having no exocyclic double bond (1). The weak -OH absorption at 3450 cm^{-1} may be caused by the presence of water in the potassium bromide, as suggested by Gronowitz (1). However, the possibility that II may exist to a small extent in the enolic form as 2-hydroxy-4-benzhydryl-5-phenylthiophene is currently under investigation using proton magnetic resonance spectroscopy.

I (a) Ar = C₆H₅(b) Ar = *o*-ClC₆H₄

II

EXPERIMENTAL (10)

Preparation of Ia.

In a 500 ml., three-necked, round bottomed flask, fitted with a condenser, stirrer and an inlet tube connected to a nitrogen supply, was placed 5 g. of α -benzylidene- γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide (7) and 4 g. of thiolacetic acid. Pyridine (20 ml.) and 10 ml. of chloroform were added and the mixture heated under reflux for 80 minutes. At the end of this period, excess solvent was removed under diminished pressure. The residue was dissolved in ether and triturated with petroleum ether. Three grams (56.3%) of an orange solid separated. It was crystallized from petroleum ether, m.p. 64° (lit. (5) m.p. $64.5\text{--}65^\circ$).

Anal. Calcd. for C₁₇H₁₂OS: C, 77.00; H, 4.60. Found: C, 76.90; H, 4.72.

4-(*o*-chlorobenzylidene)-2-phenyl- Δ^2 -thiolenes-5-one, m.p. 66° , was prepared in a similar manner.

Anal. Calcd. for C₁₇H₁₁OSCl: C, 68.34; H, 3.68. Found: C, 68.40; H, 3.70.

Reaction of α -Angelica Lactone with Thiolacetic Acid.

α -Angelica lactone (5 g.) was heated with 4 g. of thiolacetic acid as described above. The product was distilled under vacuum, b.p. $95^\circ/15\text{ mm.}$ (lit. (4) b.p. $94\text{--}96^\circ/15\text{ mm.}$). The yield was very low (10%).

To a solution of 0.5 g. of this compound was added dropwise 0.42 g. of benzaldehyde in 15 ml. of ethanolic hydrochloric acid until turbidity developed. The mixture was allowed to stand at room temperature for 3 hours. The solvent was removed and the remaining solid crystallized from alcohol, m.p. 85° (lit. (4) m.p. $85\text{--}86^\circ$).

By a similar method γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide was converted to 2-phenyl- Δ^2 -thiolenes-5-one, m.p. 80° (lit. (5) m.p. 81°). This compound was converted to Ia by reaction with benzaldehyde as described above, m.p. 64° . Mixture melting point with a sample of Ia showed no depression.

Reaction of I with benzene under Friedel-Crafts conditions.

In a 500 ml., round-bottomed flask, fitted with a mechanical stirrer, dropping funnel and reflux condenser, was placed 3.2 g. (0.042 mole) of anhydrous aluminum chloride in 65 ml. of dry, thiophene-free benzene. The mixture was cooled to 10° and stirred for 1 hour in a nitrogen atmosphere. To this solution was added 1.58 g. of 2-phenyl-4-benzylidene- Δ^2 -thiolenes-5-one (I) in 30 ml. of dry benzene and the temperature maintained at $10\text{--}20^\circ$ during the addition. The mixture turned dark red. When all of I had been added, the mixture was stirred for an additional 3 hours at room temperature. The complex was decomposed with 125 ml. of dilute (1:15) hydrochloric acid to form two clear layers. The benzene layer was separated, the aqueous layer extracted with benzene and the combined benzene layers washed with dilute hydrochloric acid and then with water until neutral to litmus. Benzene was removed under reduced pressure to give an oil which was triturated with petroleum ether. The product was crystallized from ethyl alcohol to give 1.2 g. of white crystals, m.p. $95\text{--}96^\circ$.

Anal. Calcd. for C₂₃H₁₈OS: C, 80.70; H, 5.26. Found: C, 80.58; H, 5.42.

This compound gave no depression in melting point when mixed with an authentic sample of 2-phenyl-4-benzhydryl- Δ^2 -thiolenes-5-one (II), prepared from γ -phenyl- α -benzhydryl- $\Delta^{\beta,\gamma}$ -butenolide and thiolacetic acid.

Reaction of I with phenylmagnesium bromide.

To a solution of phenylmagnesium bromide prepared from 0.45 g. of magnesium turnings and 2 ml. of bromobenzene was added over a 1 hour period 1.58 g. of compound Ia suspended in 65 ml. of ether. The mixture was heated under reflux for an additional 2 hours and then decomposed with a saturated solution of ammonium chloride. The ether layer was removed, repeatedly washed with water and dried over anhydrous magnesium sulfate. Ether was removed by evaporation on a water bath. The residual oil was triturated with petroleum ether

and the product crystallized from alcohol, m.p. 95°. Mixed melting point with II above showed no depression.

Acknowledgment.

This investigation was supported by Public Health Service Research Grant No. CA-04532-06 from the National Cancer Institute.

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- (10) All melting points were determined on a Fisher-Johns block and are uncorrected. Microanalyses were conducted by Micro-Tech Laboratories, Skokie, Illinois and infrared spectra were determined on a Perkin-Elmer 21 Spectrophotometer.

Received June 25, 1964

Chicago, Illinois 60616