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SYNTHESES OF S-PHENYL 3-OXOBUTANETHIOATES AND 2H-1-BENZOTHIOPYRAN-2-ONE DERIVATIVES (THIOCOUMARINS)

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S-Phenyl 3-oxobutanethioates, precursor for preparation of thiocoumarins, were prepared from benzenethiols and diketene in the presence of triethylamine. Cyclization of these compounds with PPA gave thiocoumarin and/or isomeric thiochromone derivatives.

2H-1-Benzothiopyran-2-ones (thiocoumarins) have been prepared by heating 2-mercaptocinnamic acids with condensing agents, but could not be obtained by the Pechmann reaction of benzenethiols.[1] K. Konishi et al. reported the convenient method to prepare thiocoumarin derivatives by the cyclization of S-phenyl 3-oxobutanethioates with PPA,[2] while the products are mostly not thiocoumarins, but isomeric thiochromones.[3] Furthermore, recently we found that the S-phenyl 3-oxobutanethioate derivatives, described in our previous paper,[3] were really isomeric arylthioisocrotonic acids (**2**) and/or arylthiocrotonic acids.

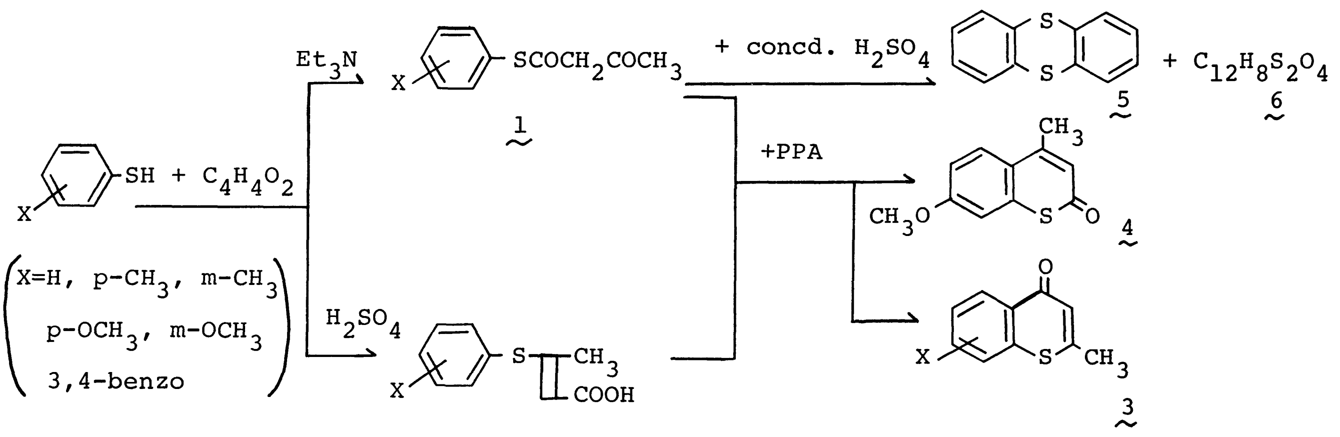
We now could prepare the S-phenyl 3-oxobutanethioates (**1**) (precursor for preparation of thiocoumarins) from benzenethiols and diketene, and studied the cyclization of these compounds with condensing agents (PPA or H_2SO_4) to prepare thiocoumarin derivatives.

S-Phenyl 3-oxobutanethioates (**1**) were obtained by the reaction of benzenethiols with diketene in the presence of triethylamine for 20 h at room temperature. Compound **1** was colorless liquid, gradually decomposed to dehydroacetic acid at room temperature, and existed in the keto-enol tautomeric mixture with the following data of NMR spectra: **1**, X=H;[4] δ(CCl_4), 1.82 and 2.09 (total 3H, each s), 3.57 and 5.39 (total ca. 1.5H, each s), 7.32 (5H,m), X=p-CH_3; δ(CCl_4), 1.90 and 2.18 (total 3H, each s), 2.38 (3H,s), 3.55 and 5.35 (total ca. 1.4H, each s) , 7.00-7.35 (4H,m), 12.35 (broad), X=m-CH_3; δ(CCl_4), 1.90 and 2.20 (total 3H, each s), 2.35 (3H, s), 3.58 and 5.35 (total ca. 1.3H, each s), 7.00-7.15 (4H,m), 12.50 (broad), X=p-OCH_3; δ(CCl_4), 1.90 and 2.18 (total 3H, each s), 3.78(

3H,s), 3.55 and 5.32 (total ca. 1.3H, each s), 6.75-7.35 (4H,m), 12.45 (broad), X=m-OCH$_3$; δ(CCl$_4$), 1.90 and 2.20 (total 3H, each s), 3.78 (3H,s), 3.58 and 5.30 (total ca. 1.3H, each s), 6.70-7.20 (4H,m), 12.00 (broad), X=3,4-benzo; δ(CCl$_4$), 1.85 and 2.12 (total 3H, each s), 3.58 and 5.38 (total ca. 1.6H, each s), 7.20-7.80 (7H,m), no enol proton was observed.

Treating **1**(X=H) with concd. H$_2$SO$_4$ for 5 h at 15°C gave thianthrene **5** (4%, mp 151-2°C, lit,$^{5)}$ 153°C) and diphenylene disulfone **6** (56%, mp>320°C, Found: C, 51.67; H, 2.97%). It might be explained that these compounds were obtained by the oxidation of diphenyl disulfide with concd. H$_2$SO$_4$, which was formed by decomposition of **1** (X=H). When **1** was treated with PPA for 1 h at 70°C, thiochromone derivative **3** was obtained in a low yield with other undetermined products (**3**, X=H, 103-104°C, 66%; X=6-CH$_3$, 121°C, 53%; X=7-CH$_3$, 98-100°C, 23%; X=6-OCH$_3$, 102-103°C, 10%; X=5,6-benzo, 126-128°C, 15%).

In the case of S-(m-methoxyphenyl) 3-oxobutanethioate **1** (X=m-OCH$_3$), thiocoumarin derivative **4** (mp 160-161°C, lit,$^{3)}$ 158-160°C) was obtained in higher yield (54%) than that from isocrotonic acid **2** (X=m-OCH$_3$). These results were summarized in Scheme I.



Scheme I

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