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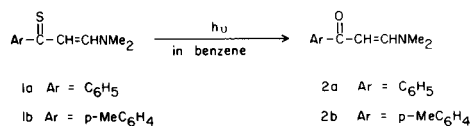
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Irradiation of  $\beta$ -aminovinyl aryl thioketones (**1a-b**) afforded  $\beta$ -aminovinyl aryl ketones (**2a-b**). 2*H*-Thiopyran derivatives (**4a-b**) were obtained when  $\beta$ -aminovinyl phenyl thioketone (**1a**) was irradiated with methyl acrylate and acrylonitrile. 4*H*-Thiopyran derivatives (**6,8**) were also obtained thermally in the reaction of  $\beta$ -aminovinyl phenyl thioketone (**1a**) and methyl propiolate and maleic anhydride.

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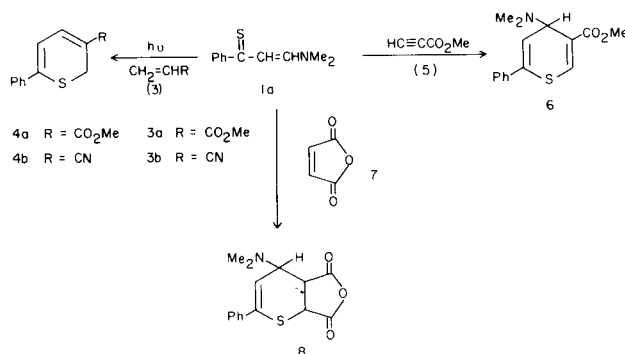
$\beta$ -Aminovinyl aryl thioketones are known to be useful synthetic intermediates and their reactivities have been extensively studied by Quiniou, *et al.*, (1). However, photochemical reaction of  $\beta$ -aminovinyl aryl thioketones have not yet received attention. We previously reported that  $\beta$ -aminovinyl ketones gave the pyrrole derivatives *via*  $\delta$ -hydrogen abstraction through a seven-membered transition state by an excited carbonyl oxygen upon irradiation (2). It is of interest to study the difference of photochemical behavior between thioketones and ketones. We report here the photochemical reactions of  $\beta$ -aminovinyl aryl thioketones (**1**).

When  $\beta$ -*N,N*-dimethylaminovinyl phenyl thioketone (**1a**) was irradiated in a Pyrex vessel with a high pressure mercury lamp in benzene,  $\beta$ -*N,N*-dimethylaminovinyl phenyl ketone (**2a**) was obtained in 28% yield. This compound was identified by direct comparison with an authentic sample (2). Irradiation of  $\beta$ -*N,N*-dimethylaminovinyl tolyl thioketone (**1b**) under the same conditions also gave  $\beta$ -*N,N*-dimethylaminovinyl tolyl ketone (**2a**) in 12% yield. These reactions also proceeded in sunlight.  $\beta$ -Aminovinyl thioketone (**1a**) was completely recovered when **1a** was irradiated in a completely degassed benzene solution or in the presence of rose bengal as a singlet oxygen sensitizer under an oxygen atmosphere. Furthermore, compound **2a** could not be detected when **1a** was treated with *m*-chloroperbenzoic acid. From these results, the formation of  $\beta$ -aminovinyl ketones (**2a-b**) can be explained in terms of photochemical oxidation of (**1a**) by oxygen dissolved in the solvent.



Irradiation of a solution of **1a** and methyl acrylate (**3a**), and acrylonitrile (**3b**) in dry benzene under an argon atmosphere gave 3-substituted-6-phenyl-2*H*-thiopyrans (**4a**) and (**4b**) in 50 and 52% yields, respectively. The pro-

ducts **4a-b** are formed *via* the Diels-Alder adducts (3). The formation of these products suggested that the same products might be produced under the effect of heat. In fact, by refluxing an equimolar mixture of **1a** and these dienophiles **3a-b** in benzene, we obtained compounds **4a** and **4b** in 47 and 20% yields, respectively. Similarly, **1a** was treated with methyl propiolate (**5**) to give 3-carbomethoxy-4-*N,N*-dimethylamino-6-phenyl-4*H*-thiopyran (**6**) in 95% yield at room temperature. Furthermore, the Diels-Alder adduct (**8**) was also obtained in 79% yield from **1a** and maleic anhydride (**7**) at room temperature. Thus  $\beta$ -aminovinyl aryl thioketone may be useful heterodienes for the Diels-Alder reaction and may be available for the synthesis of six-membered heterocyclic compounds containing the sulfur atom.



## EXPERIMENTAL

### Materials.

$\beta$ -Aminovinyl aryl thioketones (**1a-b**) were prepared according to previously reported procedures (4).

### Irradiation of $\beta$ -Aminovinyl Aryl Thioketones (**1a-b**).

A solution of  $\beta$ -aminovinyl aryl thioketone (**1**) (200 mg.) in dry benzene (40 ml.) was irradiated with a high pressure mercury lamp through a Pyrex filter for 0.5 hour at room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column. Elution with benzene-ethyl acetate (4:1) yielded  $\beta$ -aminovinyl aryl ketone (**2**). The structure of the products **2a-b** was identified by direct comparison

of their ir and nmr spectra with those of their authentic materials (2). Irradiation of the Mixture of **1a** and Methyl Acrylate (**3a**).

A solution of **1a** (200 mg.) and **3a** (110 mg.) in dry benzene (40 ml.) was irradiated under argon for 2 hours. After removal of the solvent, the residue was chromatographed on an alumina column with benzene to give 3-carbomethoxy-6-phenyl-2*H*-thiopyran (**4a**) (122 mg.), m.p. 84.5-85.5° (from ethanol); ir (potassium bromide): 1675, 1605, 1510, 1485, 1435, 1165, 1075, 760, and 685  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  3.65 (s, 2H), 3.76 (s, 3H), 6.51 (d, 1H,  $J = 6.4$  Hz), 7.1-7.7 (m, 6H).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$ : C, 67.21; H, 5.20. Found: C, 67.11; H, 5.16.

Irradiation of the Mixture of **1a** and Acrylonitrile (**3b**).

A solution of **1a** (200 mg.) and **3b** (75 mg.) in dry benzene (40 ml.) was irradiated under the same conditions as described above for 2 hours. After removal of the solvent, the residue was chromatographed on an alumina column. Elution with benzene yielded 3-cyano-6-phenyl-2*H*-thiopyran (**4b**) (97 mg.), m.p. 107-108° (from ethanol); ir (potassium bromide): 2185, 1600, 1520, 1475, 750, and 685  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  3.43 (s, 2H), 6.49 (d, 1H,  $J = 6.8$  Hz), 6.66 (d, 1H,  $J = 6.8$  Hz), 7.0-7.6 (m, 5H).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_8\text{NS}$ : C, 72.32; H, 4.55; N, 7.02. Found: C, 72.31; H, 4.54; N, 7.33.

Reaction of **1a** and Methyl Propiolate (**5**).

A solution of **1a** (200 mg.) and **5** (109 mg.) in benzene (20 ml.) was stirred at room temperature for 5 hours. After removal of the solvent, the crude product was recrystallized from benzene-hexane to give 3-carbomethoxy-4-*N,N*-dimethylamino-6-phenyl-4*H*-thiopyran (**6**) (275 mg.), m.p. 88-89°; ir (potassium bromide): 1680, 1615, 1525, 1485, 1420, 1260, 1205, 1180, 1075, 1030, 740, and 680  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$

2.18 (s, 6H), 3.74 (s, 3H), 5.47 (s, 1H), 6.53 (d, 1H,  $J = 7.4$  Hz), 7.1-7.7 (m, 6H).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$ : C, 65.42; H, 6.22; N, 5.08. Found: C, 65.69; H, 6.19; N, 5.42.

Reaction of **1a** and Maleic Anhydride (**7**).

To a solution of **1a** (120 mg.) in benzene (40 ml.) was added a solution of **7** (78 mg.) in benzene (10 ml.) at room temperature. The mixture was stirred for 5 hours and then the solvent was evaporated under reduced pressure. The crude product thus obtained was recrystallized from benzene to give **8** (237 mg.), m.p. 162-164°; ir (potassium bromide): 1770, 1680, 1650, 1605, 1525, 1425, 750, and 685  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$ : C, 62.27; H, 5.22; N, 4.84. Found: C, 62.41; H, 5.22; N, 4.48.

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