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PHOTOCHEMICAL REACTIONS—I

ADDITION OF THIOPHENOL TO BISAMIDES AND BISURETHANES OF UNSATURATED AROMATIC AND HETEROCYCLIC ALDEHYDES

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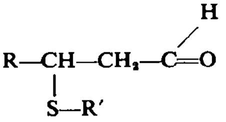
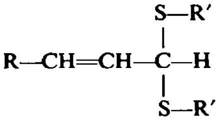
Abstract—The action of thiophenol on bisamides and bisurethanes of some unsaturated aromatic and heterocyclic aldehydes, under irradiation with UV light, results in the addition of thiophenol to the double bond and formation of the corresponding bisamides and bisurethanes of β-phenylmercaptoaldehydes.

ACCORDING to the literature, different products can result by the action of mercaptans on the aliphatic α,β-unsaturated aldehydes, depending on the nature of the catalyst used:

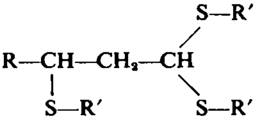

$\mathrm{R{-}\underset{S-R'}{CH}{-}CH_2{-}\overset{H}{C}{=}O}$

i

(basic catalyst)


$\mathrm{R{-}CH{=}CH{-}\overset{S-R'}{\underset{S-R'}{C}}{-}H}$

ii


$\mathrm{R{-}\underset{S-R'}{CH}{-}CH_2{-}\overset{S-R'}{\underset{S-R'}{CH}}}$

iii

(acid catalyst)

If the double bond reacts, the R′—S— group always goes in the β-position to the carbonyl group (i and iii).

However, by the action of mercaptans on cinnamaldehyde (the only unsaturated aromatic aldehyde for which the data have been found), both under ordinary conditions and in the presence of either acid[1] or basic[2] catalysts and under irradiation with UV light,[3] only the carbonyl group reacts with the formation of the corresponding bismercaptans of cinnamaldehyde, and addition to the double bond of the aldehyde does not take place.

The only case of the addition of mercaptans to cinnamaldehyde was reported by Weber,[4] who stated that ethyl mercaptan adds to the double bond of cinnamaldehyde, in the presence of sodium, giving rise to β-ethylmercapto-β-phenylpropionic aldehyde (β-ethylmercaptohydrocinnamaldehyde) in fair yield.

In order to prevent condensation reactions of the carbonyl group with mercaptan, the addition of thiophenol to cinnamyl-bisamide and bisurethane was attempted[5] without irradiation, in the presence of conc hydrochloric acid or piperidine. The addition, however, failed, and only the starting material could be isolated.

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[1] E. Baumann, *Chem. Ber.* **18**, 883 (1885).

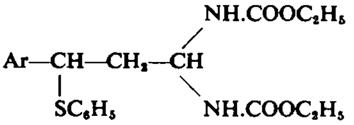
[2] J. L. Szabo and E. T. Stiller, *J. Amer. Chem. Soc.* **70**, 3667 (1948).

[3] K. Yamaghishi, *Nippon Kagaku Zasshi* **80**, 764 (1959); *Chem. Abstr.* **55**, 3493 (1961).

[4] Ger. Patent 855,704, 17.XI.1952; *Chem. Abstr.* **52**, 15565 (1958).

[5] K. Sirotanovic, M. Bajlon-Rocen and D. Galovic, *Bull. Soc. Chim. Beograd.* **25–26**, 509 (1960–1961).

But, if a few drops of conc hydrochloric acid are added to a mixture of the unsaturated aromatic aldehyde, thiophenol and urethane (in molecular ratio 1:1:2), it results in the formation of bisurethanes of β-phenylmercaptoaldehyde (I):



$$\mathrm{Ar{-}\underset{\underset{\displaystyle SC_6H_5}{|}}{CH}{-}CH_2{-}CH}\begin{matrix}\mathrm{NH.COOC_2H_5}\\ \mathrm{NH.COOC_2H_5}\end{matrix} \qquad \mathrm{I}$$

The attempts to obtain bisamides of β-phenylmercaptoaldehydes, by using acetamide instead of urethane under similar conditions, were unsuccessful. With some aldehydes bismercaptans were obtained, while with others, the bisamides of the unsaturated aldehydes resulted—with no addition of thiophenol to the double bond.

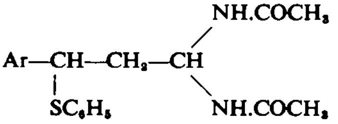
In the present work, an attempt was made to add thiophenol to bisamides and bisurethanes of some unsaturated aromatic and heterocyclic aldehydes, by irradiation with UV light. The following starting products were used:

(1) Bisamides of cinnamaldehyde, *o*-, *m*- and *p*-chlorocinnamaldehyde, *o*-, *m*- and *p*-nitrocinnamaldehyde, thiophenacrolein and furylacrolein; and

(2) Bisurethanes of cinnamaldehyde, *o*-, *m*- and *p*-chlorocinnamaldehyde, *o*-, *m*- and *p*-nitrocinnamaldehyde, and thiophenacrolein.

The reaction was carried out in the following manner: the mixture of bisamide (or bisurethane) and thiophenol, in dioxan, was irradiated with a low pressure mercury lamp (Hanau NK 6/20), for a period ranging from 10 min to 3 hr, in the presence of benzoyl peroxide or boron trifluoride. The reaction mixture was irradiated either from the side in quartz reaction vessels, or by immersing the lamp in the mixture contained in an ordinary glass vessel.

In this manner, in addition to the bisurethanes already reported, bisamides of β-phenylmercaptoaldehydes (II) were obtained, namely: *β-phenylmercaptohydrocinnamaldehyde, β-phenylmercapto-*o*-nitrohydrocinnamaldehyde, β-phenylmercapto-*p* chlorohydrocinnamaldehyde* and *β-phenylmercapto-β-thiophenylpropionaldehyde bisamides.*



$$\mathrm{Ar{-}\underset{\underset{\displaystyle SC_6H_5}{|}}{CH}{-}CH_2{-}CH}\begin{matrix}\mathrm{NH.COCH_3}\\ \mathrm{NH.COCH_3}\end{matrix} \qquad \mathrm{II}$$

Other bisamides do not react under these conditions, remaining unchanged, while bisurethanes decompose.

An attempt was also made to obtain bisamides and bisurethanes of β-phenylmercaptoaldehydes, by irradiating a mixture of the aldehyde, thiophenol and urethane (or acetamide). The reaction was carried out as above—in dioxan, in the presence of the same catalysts. The aldehydes used were: cinnamaldehyde, *o*-, *m*- and *p*-chlorocinnamaldehyde and *o*-nitrocinnamaldehyde.

In this manner it was possible to obtain only the *bisamide of β-phenylmercapto-*m*-chlorohydrocinnamaldehyde,* as well as the urethanes of β-phenylmercaptohydrocinnamaldehyde and β-phenylmercapto-*p*-chlorocinnamaldehyde.

Other aldehydes used gave bisamides or bisurethanes of the aldehydes themselves, while the addition of thiophenol to the double bond of the aldehyde did not take place.

For this investigation we prepared, in addition to the bisamides and bisurethanes already described,[5] some which have not been reported, i.e. m- and p-*nitrocinnamaldehyde*, *thiophenacrolein* and *furylacrolein bisamides*, and m- and p-*nitrocinnamaldehyde* and *thiophenacrolein bisurethanes*.

Bisurethane of furylacrolein could not be prepared by any of the methods described for the preparation of bisurethanes. In all the cases attempted resins were obtained.

On the basis of the above it can be concluded that the addition of thiophenol to the unsaturated aromatic and heterocyclic aldehydes can be achieved by irradiation with UV light, if the aldehyde carbonyl is blocked by preparing the corresponding diderivative (bisamide of bisurethane).

Studies with other mercaptans are under way.

EXPERIMENTAL

M.ps are not corrected.

Bisamide of β-phenylmercaptohydrocinnamaldehyde (II, Ar = —C_6H_5)

Cinnamaldehyde bisamide (1·2 g) and thiophenol (1·1 g) were irradiated for 3 hr in dioxan in the presence of BF_3, yielding 0·55 g (32%) of crude product, m.p. 170–173°. Recrystallized from EtOH it melted at 178–179°. (Found: N, 7·96. $C_{19}H_{22}O_2N_2S$ requires: N, 8·18%.)

Bisamide of β-phenylmercapto-o-nitrohydrocinnamaldehyde (II, Ar = *o*-$NO_2 \cdot C_6H_4$—)

The bisamide of *o*-nitrocinnamaldehyde (700 mg) and thiophenol (600 mg) were irradiated in dioxan for 3 hr in the presence of benzoyl peroxide, resulting in the isolation of 500 mg of the unchanged bisamide and 100 mg (35·7%) of the crude product m.p. = 155–156°. Recrystallized from EtOH it melted at 167°. (Found: N, 10·84. $C_{19}H_{21}O_4N_3S$ requires: N, 10·85%.)

*Bisamide of β-phenylmercapto-*m*-chlorohydrocinnamaldehyde* (II, Ar = m-$Cl \cdot C_6H_4$—)

m-Chlorocinnamaldehyde (400 mg), acetamide (300 mg) and thiophenol (300 mg) were irradiated in dioxan for 3 hr in the presence of benzoyl peroxide. After the dioxan was removed *in vacuo*, 200 mg (21%) of crude product, m.p. 154°, were obtained. Recrystallized from EtOH it melted at 189–190°. (Found: N, 7·56. $C_{19}H_{21}O_2N_2SCl$ requires: N, 7·44%.)

*Bisamide of β-phenylmercapto-*p*-chlorohydrocinnamaldehyde* (II, Ar = *p*-$Cl \cdot C_6H_4$—)

The bisamide of *p*-chlorocinnamaldehyde (660 mg) and thiophenol (300 mg) were irradiated in dioxan for 3 hr in the presence of benzoyl peroxide, yielding 550 mg (58·54%) of crude product, m.p. 165–167°. Recrystallized from EtOH it melted at 194°. (Found: N, 7·74. $C_{19}H_{21}O_2N_2SCl$ requires: N, 7·44%.)

Bisamide of β-phenylmercapto-β-thiophenylpropionaldehyde (II, Ar = C_4H_3S—)

The bisamide of thiophenacrolein (300 mg) and thiophenol (170 mg) were irradiated in dioxan for 3 hr in the presence of benzoyl peroxide, yielding 100 mg (23%) of crude product, m.p. 134°. Recrystallized from EtOH it melted at 145°. (Found: N, 7·70. $C_{17}H_{20}O_2N_2S_2$ requires: N, 8·05%.)

Bisurethane of β-phenylmercaptohydrocinnamaldehyde (I, Ar = C_6H_5—)

A. *Obtained by addition of thiophenol to bisurethane of cinnamaldehyde.* The bisurethane of cinnamaldehyde (1·5 g) and thiophenol (1·1 g) were irradiated in dioxan for 3 hr in the presence of BF_3, yielding 0·9 g (45%) of crude product, m.p. 110°. Recrystallized from abs. ether it melted at 115°.

B. *Obtained from cinnamaldehyde, thiophenol and urethane.* Cinnamaldehyde (1·3 g) urethane (1·8 g) and thiophenol (1·1 g) were irradiated in dioxan for 3 hr in the presence of BF_3. The dioxan was removed *in vacuo* and the oily residue after treatment with pet. ether gave 1·1 g (27%) of crude product, m.p. 107–109° which recrystallized from abs. ether, m.p. 115°.

A mixture of bisurethanes obtained under A. and B. above with a sample obtained previously[5] showed no depression. (Found: N, 6·99; S, 7·58. Calc. for $C_{12}H_{26}O_4N_2S$: N, 6·94; S, 7·96%.)

*Bisurethane of β-phenylmercapto-*p*-chlorohydrocinnamaldehyde* (I, Ar = p-Cl·C_6H_4—)

p-Chlorocinnamaldehyde (400 mg), urethane (500 mg) and thiophenol (300 mg) were irradiated in dioxan for 3 hr in the presence of BF_3. The dioxan was removed *in vacuo* yielding 100 mg (9%) of crude product, m.p. 95°, which recrystallized from a mixture of ether–pet. ether, m.p. 113–114°. A mixture of this product with a sample obtained previously[6] showed no depression. (Found: N, 6·83; S, 7·18. Calc. for $C_{21}H_{25}O_4N_2SCl$: N, 6·41; S, 7·33%.)

Bisamide of m-*nitrocinnamaldehyde*

m-Nitrocinnamaldehyde (3·5 g) and acetamide (4·7 g) were heated for 4 hr at 120° yielding 2·6 g (47%) of crude product, m.p. 214°, which recrystallized from EtOH, m.p. 228°. (Found: 15·43. $C_{13}H_{15}O_4N_3$ requires: N, 15·16%.)

Bisamide of p-*nitrocinnamaldehyde*

p-Nitrocinnamaldehyde (3·5 g) and acetamide (4·7 g) were heated for 4 hr at 120° yielding 4·8 g (87%) of crude product, m.p. 232°, which recrystallized from EtOH, m.p. 237°. (Found: N, 14·96. $C_{13}H_{15}O_4N_3$ requires: N, 15·16%.)

Bisamide of thiophenacrolein

Thiophenacrolein (2·7 g) and acetamide (3·5 g) were heated for 4 hr at 120° yielding 1·3 g (26%) of crude product, m.p. 195° which recrystallized from EtOH, m.p. 212°. (Found: N, 11·82. $C_{11}H_{14}O_2N_2S$ requires: N, 11·76%.)

Bisamide of furylacrolein

Furylacrolein (4·0 g) and acetamide (5·8 g) were heated for 4 hr at 120° yielding 2·0 g (28%) of crude product, m.p. 156° which recrystallized from EtOH, m.p. 188°. (Found: N, 12·76. $C_{11}H_{14}O_3N_2$ requires: N, 12·61%.)

Bisurethane of m-*nitrocinnamaldehyde*

m-Nitrocinnamaldehyde (1·8 g) and urethane (1·8 g) were dissolved in ether (20 ml) and 1–2 drops conc HCl were added to the mixture which was left overnight at room temp yielding 2·4 g (73%) of crude product, m.p. 196° which recrystallized from EtOH, m.p. 202°. (Found: N, 12·70. $C_{15}H_{19}N_3O_6$ requires: N, 12·46%.)

Bisurethane of p-*nitrocinnamaldehyde*

p-Nitrocinnamaldehyde (1·8 g) and urethane (1·8 g) were dissolved in ether (20 ml) 1–2 drops of conc HCl were added, and the mixture was left overnight at room temp. yielding 2·7 g (80%) of crude product, m.p. 173–175°, which recrystallized from EtOH, m.p. 188°. (Found: N, 12·23. $C_{15}H_{19}N_3O_6$ requires: N, 12·46%.)

Bisurethane of thiophenacrolein

Thiophenacrolein (2·7 g) and urethane (3·5 g) were dissolved in ether (20 ml) 1–2 drops of conc HCl were added, and the mixture was left 48 hr at room temp yielding 4·1 g (69%) of crude product, m.p. 132–135°. After washing several times with abs. ether it melted at 145°. (Found: N, 9·19. $C_{13}H_{18}O_4N_2S$ requires: N, 9·39%.)