

PREPARATION OF SOME 5-SUBSTITUTED
2-ARYLIMINO-4-THIAZOLIDONES

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Ten 5-sulphonamidophenyl-, four 5-phenyl-, and three 5-sulphophenyl-2-arylimino-4-thiazolidones have been prepared by utilising the reaction first reported by Mohlau and Berger.

In view of the fact that 3-ethylthiazoline-2-sulphanilamide has been reported to possess powerful growth inhibiting action of *Mycobacterium tuberculosis* (*J. Pharm. Soc. Japan*, 1952, **72**, 16), it is considered of interest to synthesise some new types of sulphonamido derivatives of thiazolidones.

The experimental procedure adopted in the present investigation is based on the observation of Mohlau and Berger (*Ber.*, 1893, **26**, 1994) and Kuhling (*Ber.*, 1895, **28**, 41, 523) that by the decomposition of a diazo compound, the organic radical formed stabilises itself by becoming attached to another carbon atom. The thiazolidone compounds prepared by the method of Rout and Mohapatra (*J. Amer. Chem. Soc.*, 1955, **77**, 2427) were coupled with diazotised sulphanilamide, employing conditions under which the diazo compounds formed were quickly decomposed with splitting of nitrogen, yielding the desired compounds. After decomposition of the diazo compound, it has been assumed that the sulphonamidophenyl group is attached to the $-CH_2$ group in 5-position of the thiazolidone nucleus, in support of which the evidences discussed by Rout and Patnaik (this *Journal*, 1955, **32**, 563) may be advanced.

Three 5-sulphophenyl- and four 5-phenyl-2-arylimino-4-thiazolidones have also been prepared by following the above method.

EXPERIMENTAL

5-Sulphonamidophenyl-2-p-tolylimino-4-thiazolidone.—Diazotised sulphanilamide, prepared by diazotising sulphanilamide (2.1 g.), was added to a solution, placed in an ice-bath, of 2-p-tolylimino-4-thiazolidone (2.5 g.) in a mixture of acetone (50 c.c.) and alcohol (10 c.c.) containing suspended crystalline sodium acetate (6 g.). A solution of cupric chloride (4 g. in 20 c.c. water) was then added dropwise during 3 to 4 hours and the whole warmed gently on a water-bath with stirring at 45° until gas evolution had ceased. The reaction mixture was then allowed to settle, the supernatant liquid decanted off and the precipitate was agitated with acetone (30 c.c.) to remove any unchanged thiazolidone. The precipitate was then collected, dried in air and finally recrystallised from alcohol in grey needles, m.p. 185°, yield 66%. (Found: N, 11.26; S, 17.22. $C_{16}H_{16}O_3N_2S_2$, requires N, 11.63; S, 17.73%.)

The properties of other 5-sulphonamidophenyl-2-arylimino-4-thiazolidones are described in Table I.

TABLE I

No.	Aryl group.	Yield.	M.P.	Cryst. form.	% Nitrogen.		% Sulphur.	
					Found.	Calc.	Found.	Calc.
1	<i>o</i> -Tolyl	60%	175°	Brown plates	11.23	11.63	17.51	17.73
2	<i>p</i> -Tolyl	60	185°	Grey needles	11.26	11.63	17.22	17.73
3	<i>o</i> -Chlorophenyl	55	145°	Yellow „	10.92	11.01	16.34	16.78
4	<i>m</i> -Chlorophenyl	50	>300°	Pale yellow flakes	10.64	11.01	16.40	16.78
5	<i>m</i> -Nitrophenyl	50	105°	Dark brown needles	10.12	10.11	15.92	16.32
6	<i>p</i> -Nitrophenyl	55	>300°	Yellow „	10.27	10.71	15.86	16.32
7	<i>o</i> -Carboxyphenyl	60	130°	Grey „	10.28	10.74	16.13	16.37
8	<i>m</i> -Carboxyphenyl	55	210°	Grey flakes	10.36	10.74	16.24	16.37
9	<i>p</i> -Carboxyphenyl	63	217°	Grey needles	10.45	10.74	16.14	16.37
10	α -Naphthyl	60	160°	Brown „	8.38	8.88	13.14	13.53

5-Sulphophenyl-2-phenylimino-4-thiazolidone.—Diazotised sulphanilic acid, prepared by diazotising sulphanilic acid (2.1 g.), was added to an ice-cold solution of 2-phenylimino-4-thiazolidone (2.34 g.) in acetone (50 c.c.) in which crystallised sodium acetate (6 g.) was suspended. A solution of cupric chloride (4 g. in 20 c.c. water) was added to it dropwise with constant stirring, and the whole warmed on a water-bath. The product separating as a buff-coloured copper salt was allowed to settle, the supernatant liquid decanted off and the precipitate agitated with acetone (30 c.c.). The precipitate, after being air-dried, was digested with NaOH solution (2*N*) in which it dissolved, the copper content, however, being precipitated. After filtration the alkaline solution was acidified with HCl, furnishing the final product as light brown crystals, m.p. 225°, yield 63%. (Found: S, 17.94. $C_{15}H_{12}O_4N_2S_2$ requires S, 18.39%). The properties of other 5-sulphophenyl-2-arylimino-4-thiazolidones are described in Table II.

TABLE II

No.	Aryl group.	Yield.	M.P.	Cryst. form	% Sulphur.	
					Found.	Calc.
1	Phenyl	63%	226°	Light brown needles	17.94	18.39
2	<i>p</i> -Nitrophenyl	56	207°	Yellowish brown needles	15.83	16.28
3	β -Naphthyl	68	93°	Brown needles	15.67	16.08

5-Phenyl-2-phenylimino-4-thiazolidone.—Diazotised aniline was treated with 2-phenylimino-4-thiazolidone in acetone in presence of crystallised sodium acetate as described above. The product was then decomposed by adding a solution of cupric chloride and the product was isolated in the manner described earlier which separated as light yellow needles, m.p. 154°, yield 68%. (Found: S, 11.63. $C_{15}H_{12}ON_2S$ requires S, 11.94%).

The properties of other 5-phenyl-2-phenylimino-4-thiazolidones are described in Table III.

TABLE III

No.	Aryl group.	Yield.	M.P.	Cryst. form	% Sulphur.	
					Found.	Calc.
1	Phenyl	68%	154°	Yellow needles	11.63	11.94
2	<i>m</i> -Chlorophenyl	65	161°	Yellow flakes	10.12	10.56
3	<i>p</i> -Chlorophenyl	64	267°	Yellow needles	10.24	10.56
4	<i>p</i> -Nitrophenyl	73	216°	Brown „	9.85	10.23

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