

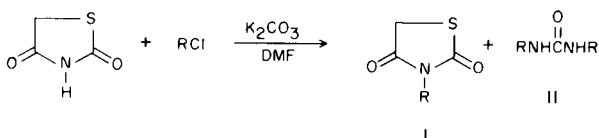
Ureas From 2,4-Thiazolidinedione

Gether Irick, Jr.

Research Laboratories, Tennessee Eastman Company,
Division of Eastman Kodak Company, Kingsport, Tennessee 37662

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The 2,4-thiazolidinedione moiety has been used as a substituent on dyes to impart desirable fastness properties (1-3). During the preparation of a number of 3-alkyl-2,4-thiazolidinedione dye couplers, it was observed that the yields decreased drastically with increased reaction temperatures and/or increased reaction times. The purpose of this paper is to describe the novel urea synthesis which resulted from these observations.



2,4-Thiazolidinedione is alkylated readily at the nitrogen when heated with alkyl chlorides for one hour at 130° in DMF/potassium carbonate (1-3). A modification of this procedure (142-145°/five minutes) was used for the preparation of the 3-alkyl-2,4-thiazolidinediones (Ia-c) in Table I. Prolonged reaction at temperatures above 120° gave decreased yields of Ia-c and formed higher melting products; nmr spectra, mass spectra, infrared spectra, and elemental analyses of these products were consistent with the 1,3-dialkylurea structure II. The yields of ureas IIa-c were 30 to 38% after four hour's reaction at 143-146° and were not increased significantly by longer or shorter reaction times. Moreover, when I was isolated and heated at 145° in DMF/potassium carbonate, it failed to yield detectable (infrared) quantities of II. The possibility of urea as an impurity in the starting 2,4-thiazolidinedione was excluded on the basis of infrared spectra obtained. The mechanism of this reaction is presently uncertain.

EXPERIMENTAL

Melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were

determined in potassium bromide on a Perkin-Elmer Model 421 spectrophotometer. Ultraviolet spectra were determined with either a Cary Model 14 or a Perkin-Elmer Model 450 spectrophotometer. Nmr analyses were determined with a Varian A-60 spectrometer. Mass spectral analyses were determined with a Consolidated Electro-dynamics Corp. Model 21-110B spectrometer. Elemental analyses were performed in these laboratories.

3-[2-(*N*-Ethylanilino)ethyl]-2,4-thiazolidinedione (Ia).

A mixture of *N*-(2-chloroethyl)-*N*-ethylaniline (36.7 g., 0.2 mole), 2,4-thiazolidinedione (23.6 g., 0.2 mole), potassium carbonate (27.6 g., 0.2 mole), and dry DMF (200 ml.) was refluxed gently (142-145°) for five minutes, allowed to cool to 100°, and poured into one l. of water. The oil, which separated from the aqueous layer, solidified after one hour.

Recrystallization of the crude product from ethanol (450 ml.) afforded 30.4 g. (58% yield) of Ia, m.p. 102-105°. An additional recrystallization from ethanol/methyl cellosolve gave the analytical sample, needles, m.p. 105-106°.

1,3-Bis[2-(*N*-ethylanilino)ethyl]urea (IIa).

A mixture of *N*-(2-chloroethyl)-*N*-ethylaniline (36.7 g., 0.2 mole), 2,4-thiazolidinedione (23.6 g., 0.2 mole), potassium carbonate (27.6 g., 0.2 mole), and dry DMF (200 ml.) was refluxed (146°) for four hours and then poured into one l. of water. Solids were filtered and recrystallized from ethanol to afford 13.4 g. (38% yield) of IIa, m.p. 141-145°. An additional recrystallization from ethanol/methyl cellosolve gave the analytical sample, m.p. 143-145°; nmr (deuteriochloroform) δ 1.25 (t, 3H), 3.3 (q, 2H), 3.31 (m, 4H), 5.7 (broad, 2H), 6.56 (m, 3H), 7.1 (m, 2H), 7.1 (m, 2H); mass spectrum (70 eV) m/e 163, 148, 134, 120.

Acknowledgement

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REFERENCES

- (1) M. A. Weaver and D. J. Wallace (to Eastman Kodak Company, U. S. Patent 3,349,076 (1967).
- (2) M. A. Weaver and D. J. Wallace (to Eastman Kodak Company, U. S. Patent 3,370,055 (1968).
- (3) M. A. Weaver and D. J. Wallace (to Eastman Kodak Company, U. S. Patent 3,423,394 (1969).

TABLE I
Physical and Spectral Data for 2,4-Thiazolidinediones I

Compound	Yield, %	M.p., °C.	Analysis, %		λ max, nm	Ultraviolet (a) ε, M ⁻¹ cm ⁻¹	Infrared (b), cm ⁻¹		
			Calc'd.	Found			C=O	aromatic	
Ia	58	105-106	C 59.07	59.05	302	2,221	1745 (m)	1665 (s)	1596 (m)
			H 6.10	6.12	259	15,373			
			N 10.60	10.39					
Ib	66	61-62 (c)	C 60.40	60.40	296	2,721	1748 (m)	1680 (s)	1594 (s)
			H 6.52	6.49	259	14,614			
			N 10.06	10.01					
Ic	68	180-181	C 65.03	65.07	304	2,798	1750 (m)	1680 (s)	1599 (m)
			H 7.28	7.21	262	11,471			
			N 8.43	8.22					

(a) Determined in methylene chloride. (b) Determined in KBr. (c) Lit. (2) m.p. 59-60°, no analyses reported.

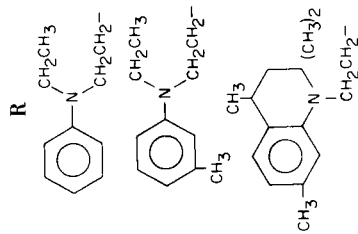


TABLE II

Physical and Spectral Data for Ureas II

Compound	Yield %	M.p., °C.	Analysis, %		λ max, nm	Ultraviolet (a) ε, M ⁻¹ cm ⁻¹	Infrared (b), cm ⁻¹		
			Calc'd.	Found			C=O	aromatic	
IIa	38	143-145	C 71.15	71.26	306	4,639	1617 (s)	1596 (s)	1580 (s)
			H 8.53	8.48	252	29,737			
			N 15.81	15.53					
IIb	36	147-149	C 72.21	71.97	305	4,474	1617 (s)	1596 (s)	1573 (s)
			H 8.96	8.87	262	26,677			
			N 14.65	14.38					
IIc	30	217-218	C 75.87	75.57	309	5,332	1620 (s)	1605 (s)	1568 (s)
			H 9.45	9.36	265	20,693			
			N 11.42	11.03					

(a) Determined in methylene chloride. (b) Determined in KBr.

