

The Synthesis of Benzo[*c*]cinnoline Dioxides

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Sir:

Benzo[*c*]cinnolines (4) normally are prepared by reduction of 2,2'-dinitrobiphenyls (1). E. Täuber (2) discovered and investigated this earlier and found that the dioxide (2) (3) and the monoxide (3) were intermediates in this reaction.

Recent investigations by Suzuki, *et al.*, (4,5) in the pyridazine, cinnoline and benzo[*c*]cinnoline series have

shown that the preparation of these dioxides by oxidation of the monoxides gives the expected products, but only in poor yield.

We now wish to report a general method for the preparation of benzo[*c*]cinnoline dioxides by catalytic reduction of 2,2'-dinitrobiphenyls (5) in ethanol containing alkali and W6- or W7-Raney Nickel (6) (6-10 weeks

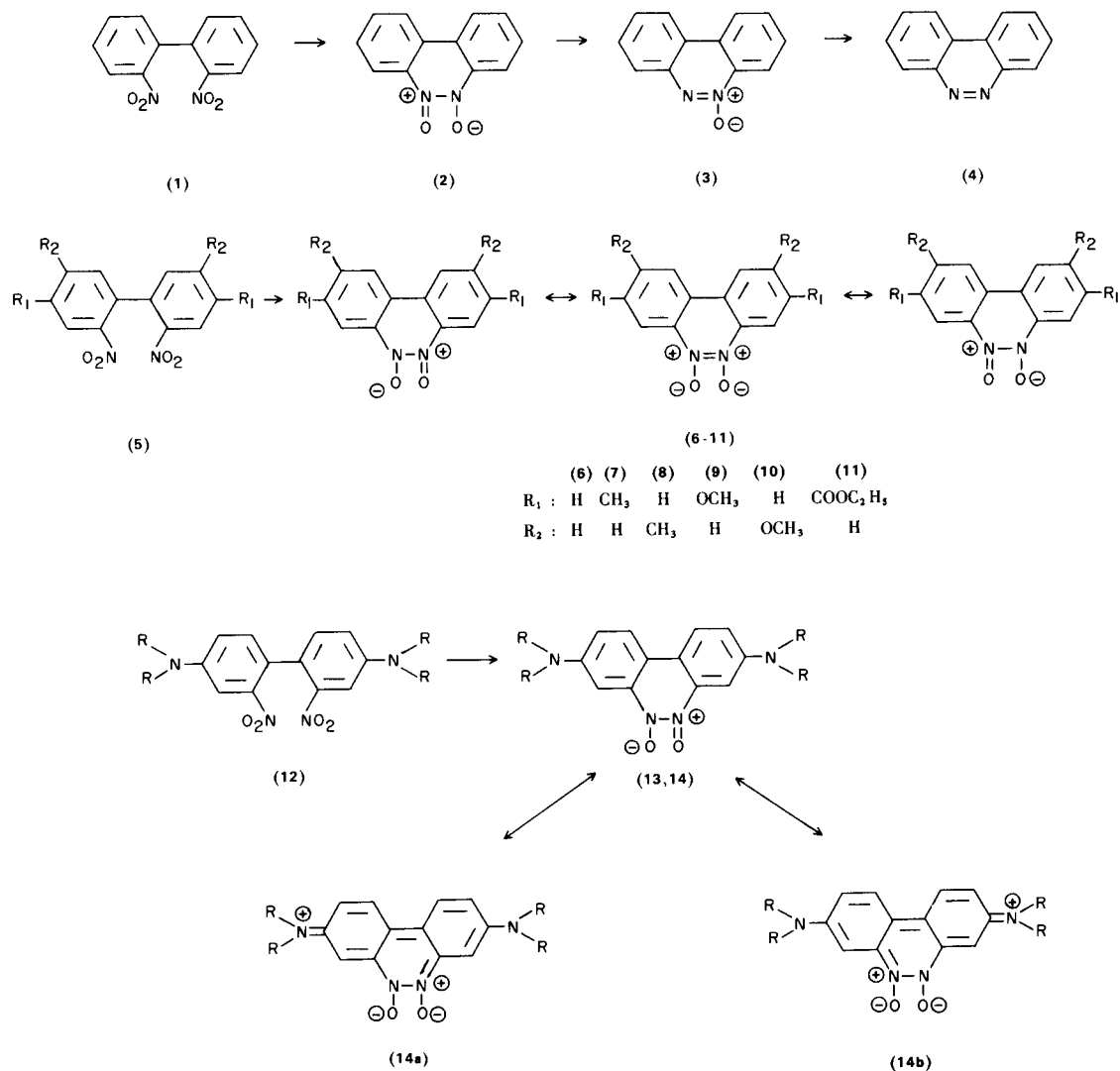


TABLE I

Com- pound	R ₁	R ₂	Cata- lyst	Purifi- cation	Yield %	M.P. °C	Halfwave potential -E _{1/2} (a)	λ max (mμ)	UV-Absorption maxima (b) ε	Analyses					
										Calcd. C	H	N	Found C	H	N
6	H	H	W6	recryst.	56	249-250 dec. (c)	0.41, 0.62, 1.16 (d)	214, 221, 240, (250), 258, (269), 291, 304, 345	14,350, 13,050, 30,500, (3,315), 37,850, (22,000), 13,150, 13,150, 1,150	67.92	3.80	13.20	67.70	3.63	13.19
7	CH ₃	H	W6	recryst.	50	265-266 dec.	0.34, 0.53, 0.70, 0.97	(211), 216, 224, (242), (256), 262, (275), (293), (307), 347, (385), (407)	(7,200), 8,600, 7,900, (25,750), (40,000), 43,850, (32,650), (14,800), (10,250), 11,000, (2,700), (1,750)	69.99	5.03	11.66	69.75	4.94	11.48
8	H	CH ₃	W6	column	68	260-261 dec. (c)	0.68, 1.02	(207), 211, 217, 223, 242, (251), 258, (267), 293, 304, 347, (379), (398)	(550), 4,200, 5,600, 3,100, 28,750, (32,100), 40,700, (24,400), 15,200, 16,100, 12,900, (2,800), (950)	69.99	5.03	11.66	69.88	5.23	11.71
9	OCH ₃	H	W7	recryst.	50	256-257 dec.	0.66, 0.98	(224), 268, (283), 349, 410, 430	(8,600), 41,400, (31,900), 8,600, 3,200, 3,200	61.76	4.44	10.29	61.69	4.43	9.98
10	H	OCH ₃	W7	column	55	255 dec. 1.40	0.40, 0.70, 1.06, 1.40	212, 268 315, 358	17,800, 42,000, 19,800, 13,700	61.76	4.44	10.29	61.77	4.69	9.94
11	COOC ₂ H ₅	H	W7	recryst.	60	>290 dec.	0.51, 0.75	218, 240, (265), 276, 292, (314), 347	8,300, 23,100, (28,350), 39,400, 46,850, (13,700), 8,000	60.67	4.53	7.86	60.40	4.35	8.11

(a) These observations were taken with a Sargent Polarograph Model 16. The polarographic halfwave potentials were measured in 40% ethanol. Potassium chloride was used as the electrolyte and methylcellulose (0.005%) for maximum depression. (b) These observations were recorded with Cary Models 14 and 15 UV Spectrophotometers. (c) E. Täuber (1) gives m.p. 240° and later investigators found 231-233° dec., (5), 233-236° dec., (8), 234-246° dec., (9,10). (d) S. D. Ross, *et al.*, ref. 8, found one halfwave at $E_{1/2} = 0.80$ ("pH, 5.2"). (e) L. Meyer (11) reported a melting point of 128° dec. () Shoulders in the UV absorption data are in parentheses.

TABLE II

Com- pound	R	Cata- lyst	Purifi- cation	Yield %	M.P. °C	Halfwave potential -E _{1/2} (a)	λ max (mμ)	UV-Absorption maxima (b) ε	Analysis					
									Calcd. C	H	N	Found C	H	N
13	H	W7	recryst.	40	>270 dec. (c)	0.71, 1.08	222, 255, 305, (320), 496	1,200, 1,350, 36,300, (21,500), 2,650	59.50	4.16	23.13	59.69	4.31	22.70
14	C ₂ H ₅	W7	recryst.	46	233-234 dec.	1.11	230, 257, 319, 335, (350), 533	16,100, 16,250, 59,250, 54,450, (37,310), 3,600	67.77	7.39	15.81	67.54	7.57	15.99

(a) These observations were taken with a Sargent Polarograph Model 16. The polarographic halfwave potentials were measured in 40% ethanol. Potassium chloride was used as the electrolyte and methylcellulose (0.005%) for maximum depression. (b) These observations were recorded with the Cary Model 14 UV Spectrophotometer. (c) Without melting. () Shoulders in the UV absorption data are in parentheses.

old) (7) as catalyst. These data are recorded in Table I.

In the course of the hydrogenation, the reaction product crystallized and was isolated by extraction with chloroform and evaporation to give the crude material, containing a little monoxide. The mixture was further purified by recrystallization or column chromatography. The nearly colorless to yellow compounds were found to be homogeneous when examined by TLC in two different solvent systems.

During further study of this reaction in the dinitrobenzidine series (12) some red-violet compounds separated which were shown to be the dioxides (13,14). The electronic absorption data at 496 $m\mu$ for compound 13 and 533 $m\mu$ for compound 14 prompted us to formulate the mesomeric structures 14a and 14b in addition to structures 6-11. Data on compounds 13 and 14 are recorded in Table II.

In order to investigate the interrelations among the dioxides (13, 14), the monoxides and the corresponding benzo[c]cinnolines, we have prepared these compounds also and studied the ultraviolet spectra. These results and the infrared analysis studies will be reported at a later date.

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