Reduction of α,β-Unsaturated Nitroalkenes with Borane and Borohydrides. A Convenient Route to 3-Nitro-, 3-Hydroxylamino-, and 3-Amino-2*H*-1-benzopyran Derivatives

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Received November 24, 1986

The borohydride catalyzed borane reduction of 3-nitrochromenes provided a facile route to a variety of 3-hydroxylamino- **5** and 3-amino-2*H*-1-benzopyranes **6**. Reduction with methoxyborohydride species, on the other hand, provided 3-nitrochromans **2,4**.

J. Heterocyclic Chem., **24**, 767 (1987).

Nitro-2*H*-1-benzopyrans have attracted attention in recent years because of their potential use as precursors to a variety of medicinally important 2*H*-1-benzopyran derivatives [1] such as flavonols [2], amines [3], oximes [4] *etc.* Surprisingly, little is known about 3-nitrochromans [5,6], in spite of extensive reports on the synthesis [7,8] and biological activity of 3-nitrochromenes [9-12]. The simplest approach to nitrochromans involves the reduction of the corresponding chromenes [13,14] by catalytic hydrogenation or hydride reduction. However, the reduction of 3-nitrochromenes results in the formation of chromanamines [6,15,16]. Consequently, the nitrochromans prepared to date have a nitro group attached to the aromatic ring [5]; the only exception being intermediates in the synthesis of 3-aminoflavans [6] and a 2-methyl-3-nitrochroman [17].

3-Chromanamines exhibit a variety of pharmacological properties whereas the 2- and 4-isomers appear to be physiologically inactive [18]. The principal route to 3-chromanamines involves the reduction of 3-nitro-2*H*-1-benzopyrans [15], 3-amino-4-chromanone hydrochlorides [19], and 3-amino-4-chromanols [19,20]. Interestingly, only

Table I

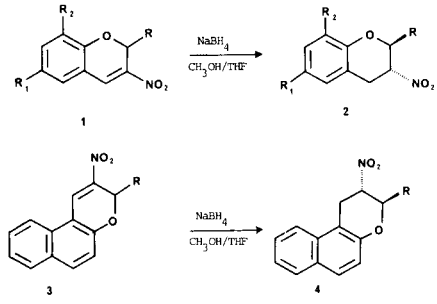
Synthesis of 2-Aryl-3-nitrochroman Derivatives from **1**

Compound No.	R_1	R_2	R	Yield [a] [%]	mp [°C] (solvent)	Molecular Formula	Analyses (%) Calcd./Found C	H	N
2a	H	H	Phenyl	65	170-171 (CH_3OH)	$C_{15}H_{13}NO_3$	70.59 70.23	5.10 5.15	5.49 5.41
2b	H	OCH_3	Phenyl	82	205-206 (CH_3OH)	$C_{16}H_{15}NO_4$	67.37 67.37	5.26 5.44	4.91 4.76
2c	Cl	H	Phenyl	80	126 (Ether)	$C_{15}H_{12}ClNO_3$	62.19 61.92	4.14 4.24	4.84 4.60
2d	NO_2	H	Phenyl	51	174-175 (Ether)	$C_{15}H_{12}N_2O_5$	60.00 59.73	4.00 3.79	9.33 8.75
2e	H	H	3,4-Diethoxyphenyl	67	143-144 (CH_3OH)	$C_{19}H_{21}NO_5$	66.47 66.28	6.12 6.03	4.08 3.96
2f	H	OCH_3	3,4-Diethoxyphenyl	81 [b]	147-148 (CH_3OH)	$C_{20}H_{23}NO_6$	64.34 63.96	6.17 5.91	3.75 3.48
2g	H	H	1-Naphthyl	87	190-191 (CH_3OH/THF)	$C_{19}H_{15}NO_3$	74.95 74.95	4.92 4.79	4.59 4.36
2h	H	OCH_3	1-Naphthyl	55	173-174 (CH_3OH)	$C_{20}H_{17}NO_4$	71.64 71.58	5.07 5.17	4.18 3.90
2i	H	H	2-Naphthyl	79	195-196 (CH_3OH/THF)	$C_{19}H_{15}NO_3$	74.75 74.77	4.92 5.11	4.59 4.26
2j	Cl	H	1-Naphthyl	77	176-177 (CH_3OH/THF)	$C_{19}H_{14}ClNO_3$	67.17 67.12	4.12 4.12	4.12 3.98
2k	NO_2	H	1-Naphthyl	72	187-189 (CH_3OH)	$C_{19}H_{14}N_2O_5$	65.14 65.31	4.00 4.07	8.00 7.97
4a	–	–	–	85	183-184 (Ether)	$C_{19}H_{15}NO_3$	74.75 74.35	4.92 5.13	4.59 4.40
4b	–	–	–	74	224-225 (Ether/THF)	$C_{23}H_{17}NO_3$	77.75 77.50	4.79 5.06	3.94 3.84

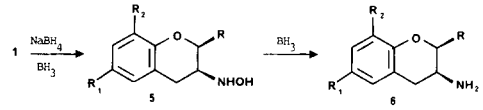
[a] Isolated and unoptimized yields. [b] Due to the moderate solubility of the chromene, 50 ml of solvent was used and the reaction time was 55 minutes.

one report has appeared which describes the preparation of 3-amino-2-arylphenylchroman derivatives by the sodium borohydride reduction of the corresponding 3-nitrochroman [6]. Our continued interest in benzopyran derivatives [4,7,8,21] prompted us to develop methods to synthesize 3-nitro-, 3-amino- and the previously unknown 3-hydroxylamino-2*H*-1-benzopyran derivatives.

In a preliminary communication, we reported that 3-nitrochromenes could be reduced to the corresponding 3-nitrochromans [21] using sodium borohydride in a mixed solvent system of methanol-tetrahydrofuran. We find that the reaction is a general one and can be utilized to synthesize a wide variety of 2-aryl-3-nitro-3,4-dihydro-2*H*-1-benzopyrans **2** and **4**. *In-situ* generated methoxyborohydride species are implicated as the reducing agent in this facile reaction which provide good yields of single isomers. The high stereoselectivity of the reduction was ascertained by the fact that the ^1H nmr spectra displayed only the characteristic ($J_{2,3}$ = ~7 Hz) coupling typical of the thermodynamically more stable *trans*-chromans [16,23]. Furthermore, only one set of carbon resonances were observed for the chroman ring. Our results are summarized in Tables 1 and 2.



The reduction of 3-nitrochromenes by a borane borohydride system yields the corresponding hydroxylamine **5** derivative which can be converted into the desired amine **6** upon further reaction with borane. We have used the



reaction sequence to synthesize a variety of 3-hydroxylamino- and 3-amino-2*H*-1-benzopyrans. Our results are summarized in Tables 3, 4, 5, and 6.

Table II

Spectral Data of 2-Aryl-3-nitrochroman Derivatives [a]

Compound No.	^1H-NMR δ 2-H	3-H	4-H	Other Signals		^{13}C-NMR δ 2-C	3-C	4-C	Other Signals	
2a	5.42 (d, $J_{2,3}$ = 7.9 Hz, 1H)	5.13 (m, 1H)	3.47 (m, 1H)	7.74-6.9 (m, 9H, Ar-H)		78.05	84.03	29.83	–	
2b	5.56 (d, $J_{2,3}$ = 7.0 Hz, 1H)	5.05 (m, 1H)	3.42 (m, 2H)	3.85 (s, 3H, OCH_3)	7.7-6.7 (m, 8H, Ar-H)	77.97	83.74	28.86	56.08 (OCH_3)	
2c	5.48 (d, $J_{2,3}$ = 7.5 Hz, 1H)	5.02 (m, 1H)	3.37 (m, 2H)	7.5-6.8 (m, 8H, Ar-H)		78.02	83.33	28.94	–	
2d	5.47 (d, $J_{2,3}$ = 7.2 Hz, 1H)	5.02 (m, 1H)	3.40 (m, 2H)	7.7-6.8 (m, 8H, Ar-H)		78.32	82.35	27.96	–	
2e	5.27 (d, $J_{2,3}$ = 8.3 Hz, 1H)	5.02 (m, 1H)	3.47 (m, 2H)	4.07 (q, 4H, 2 x OCH_2)	1.43 (t, 6H, 2 x CH_3) 7.4-6.7 (m, 7H, Ar-H)	78.10	84.22	28.32	14.8 (CH_3)	64.69 (OCH_2) 64.56 (OCH_2)
2f	5.50 (d, $J_{2,3}$ = 6.0 Hz, 1H)	5.35 (m, 1H)	3.42 (m, 2H)	4.05 (q, 2H, OCH_2) 3.78 (s, 3H, OCH_3)	4.03 (q, 2H, OCH_2) 1.30 (t, 6H, CH_3) 7.1-6.75 (m, 6H, Ar-H)	78.97	84.69		15.73 (CH_3) 56.85 (OCH_3)	65.89 (OCH_2) 65.81 (OCH_2)
2g	6.41 (d, $J_{2,3}$ = 5.9 Hz, 1H)	5.38 (m, 1H)	3.41 (m, 2H)	8.2-6.9 (m, 11H, Ar-H)		75.56	82.06	28.24		
2h	6.63 (d, $J_{2,3}$ = 4.6 Hz, 1H)	5.32 (m, 1H)	3.34 (m, 2H)	8.2-6.7 (m, 10H, Ar-H)	3.87 (s, 3H, OCH_3)	75.50	81.76	27.02	56.16 (OCH_3)	
2i	5.58 (d, $J_{2,3}$ = 7.9 Hz, 1H)	5.15 (m, 1H)	3.51 (m, 2H)	8.0-6.9 (m, 11H, Ar-H)		78.26	83.98	29.91		
2j	6.49 (d, $J_{2,3}$ = 5.1 Hz, 1H)	5.33 (m, 1H)	3.31 (m, 2H)	8.2-6.8 (m, 10H, Ar-H)		75.58	81.30	27.15		
2k	6.76 (d, $J_{2,3}$ = 4.5 Hz, 1H)	5.37 (m, 1H)	3.35 (m, 2H)	8.3-7.0 (m, 10H, Ar-H)		76.15	80.38	26.01		

[a] The nmr spectra were recorded in deuteriochloroform except for **2f** which was obtained at 45° in deuterioacetone.

Table III

Synthesis of 2-Aryl-3-hydroxylaminochroman Derivatives from **1**

Compound No.	R_1	R_2	R	Yield [a] [%]	mp [b] [°C]	Molecular Formula	Analyses (%) Calcd./Found C	H	N
5a	H	H	Phenyl	83	94-96 [c]	$C_{15}H_{15}NO_2$	74.67	6.27	5.81
							74.84	6.45	5.85
5b	H	OCH_3	Phenyl	74	132-133	$C_{16}H_{17}NO_3$	70.83	6.32	5.16
							70.93	6.23	5.27
5c	Cl	H	Phenyl	78	136-138	$C_{15}H_{14}ClNO_2$	65.34	5.12	5.08
							65.46	5.26	4.97
5d	H	H	*p*-Isopropylphenyl	74	110-112	$C_{18}H_{21}NO_2$	76.29	7.47	4.94
							76.06	7.64	5.04
5e	H	H	3,4-Diethoxyphenyl	77	118-120	$C_{19}H_{23}NO_4$	69.28	7.04	4.25
							69.65	7.09	4.19
5f	NO_2	H	Phenyl	84	154-156	$C_{15}H_{14}N_2O_4$	62.93	4.93	9.79
							62.54	5.05	9.38
5g	H	H	1-Naphthyl	70	152-154	$C_{19}H_{17}NO_2$	78.33	5.88	4.81
							78.14	5.95	4.79

[a] Isolated and unoptimized yield. [b] Uncorrected mp, recrystallization solvent ethanol. [c] Recrystallized from ether-petroleum ether (1:1).

Table IV

Spectral Data of 2-Aryl-3-hydroxylaminochroman Derivatives

	^{1}H-NMR δ				^{13}C-NMR δ				
Compound No.	2-H	3-H	4-H	Other Signals	2-C	3-C	4-C	Other Signals	
5a	5.24 (d, $J_{2,3}$ = 2.2 Hz, 1H)	3.47 (m, 1H)	2.98 (d, $J_{3,4}$ = 2.7 Hz, 2H)	7.37-6.84 (m, 9H, Ar-H)	76.86	57.81	27.69		
5b	5.35 (d, $J_{2,3}$ = 2.2 Hz, 1H)	3.56 (m, 1H)	2.93 (d, $J_{3,4}$ = 4.17 Hz, 2H)	7.36-6.71 (m, 8H, Ar-H) 3.85 (s, 3H, OCH_3)	77.1	57.60	27.31	56.14 (OCH_3)	
5c	5.19 (d, $J_{2,3}$ = 2.2 Hz, 1H)	3.48 (m, 1H)	2.92 (d, $J_{3,4}$ = 3.52 Hz, 2H)	7.36-6.78 (m, 8H, Ar-H)	77.1	57.44	27.53		
5d	5.20 (d, $J_{2,3}$ = 2.2 Hz, 1H)	3.49 (m, 1H)	2.94 (d, $J_{3,4}$ = 4.18 Hz, 2H)	7.26-6.74 (m, 8H, Ar-H) 1.25 [d, 6H, $CH(CH_3)_2$]	77.05	57.76	27.64	33.98 (CH)	24.12 $CH(CH_3)_2$
5e	5.17 (d, $J_{2,3}$ = 2.3 Hz, 1H)	3.47 (m, 1H)	2.93 (d, $J_{3,4}$ = 4.00 Hz, 2H)	7.2-6.39 (m, 7H, Ar-H) 4.07 (m, 4H, 2 x OCH_2) 1.43 (t, 6H, 2 x CH_3)	77.1	57.81	27.48	65.0 ($-OCH_2$)	14.89 (CH_3)
5f	5.37 (d, $J_{2,3}$ = 2.2 Hz, 1H)	3.60 (m, 1H)	3.05 (d, $J_{3,4}$ = 3.74 Hz, 1H)	8.0-6.93 (m, 8H, Ar-H)	78.05	56.98	27.61		
5g	5.81 (s, 1H)	3.48 (m, 1H)	2.93 (d, $J_{3,4}$ = 2.63 Hz, 1H)	7.95-6.75 (m, 11H, Ar-H)	74.64	56.22	27.96		

The stereoselectivity of the borohydride mediated, borane reductions is rather remarkable. In contrast to the reductions utilizing borane in methanolic-THF, only *cis*-2-aryl-3-amino derivatives are obtained as evidenced by the H_2-H_3 coupling constants ($J_{2,3}$ <2.3 and, often, 0). Examination of Dreiding models of the intermediate acinitro compounds leads to the conclusion that the reduction occurs with the molecule in the boat conformation and with the 2-aryl substituent forced into the pseudo axial position by repulsive interactions with the rigid NO_2 function of the acinitro group. Subsequent hydride reduction *via* a pseudo equatorial approach of hydride would then lead to the observed *cis* product.

EXPERIMENTAL

Melting points are uncorrected. The nmr spectra were recorded on a JEOL-FX90Q and Nicolet NT-200 spectrometer and referenced to TMS. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Table V

Synthesis of 2-Aryl-3-aminochroman Derivatives from **1**

Compound No.	R_1	R_2	R	Yield [a] [%]	mp [°C] [b]	Molecular Formula	Analyses (%) Calcd./Found C	H	N
6a	H	H	Phenyl	89	261-263	$C_{15}H_{15}NO\cdot HCl$	68.83	5.73	5.40
							68.75	6.01	5.30
6b	H	OCH_3	Phenyl	94	260-262	$C_{16}H_{17}NO_2\cdot HCl$	65.86	6.22	4.80
							65.61	6.41	4.81
6c	Cl	H	Phenyl	68	88-89 [c]	$C_{15}H_{14}ClNO$	69.36	5.43	5.39
							69.58	5.58	5.37
6d	H	H	*p*-Isopropylphenyl	83	237-239	$C_{18}H_{21}NO\cdot HCl$	71.16	7.30	4.61
							71.25	7.16	4.63
6e	H	H	3,4-Diethoxyphenyl	87	224-226	$C_{19}H_{23}NO_3\cdot HCl$	65.23	6.91	4.00
							65.12	7.07	4.08
6f	H	H	1-Naphthyl	74	263-265	$C_{19}H_{17}NO\cdot HCl$	73.18	5.82	4.49
							73.25	6.05	4.48
6g	H	OCH_3	1-Naphthyl	92	262-264	$C_{20}H_{19}NO_2\cdot HCl$	70.27	5.90	4.01
							70.12	6.00	4.35

[a] Isolated and unoptimized yield of free base. [b] Uncorrected mp of hydrochloride salts recrystallized from ethanol-ether. [c] Free base, recrystallized from 90% ethanol.

Table VI

Spectral Data of 2-Aryl-3-aminochroman Derivatives [a]

Compound No.	^{1}H-NMR δ 2-H	3-H	4-H	Other Signals	^{13}C-NMR δ 2-C	3-C	4-C	Other Signals	
6a	5.43 (d, $J_{2,3}$ = 1.54 Hz, 1H)	4.00 (m, 1H)	3.42 (m, 2H)	8.33 (br s, 3H, NH_3) 7.61-6.92 (m, 9H, Ar-H)	75.23	47.33	27.04		
6b	5.38 (s, 1H)	3.97 (m, 1H)	3.34 (m, 2H)	8.27 (br s, 3H, NH_3) 7.57-6.70 (m, 8H, Ar-H) 3.79 (s, 3H, OCH_3)	75.22	47.08	27.02	55.58 (OCH_3)	
6c [b]	5.45 (d, $J_{2,3}$ = 0.88 Hz, 1H)	4.00 (m, 1H)	3.36 (m, 2H)	3.88 (brs, 3H, NH_3) 7.60-6.90 (m, 8H, Ar-H)	75.38	46.78	28.41		
6d	5.41 (s, 1H)	3.96 (m, 1H)	3.29 (m, 2H)	8.36 (br s, 3H, NH_2) 7.50-6.80 (m, 8H, Ar-H) 2.91 (m, 1H, $CH(CH_3)_2$ 1.22 (d, 6H, $CH(CH_3)_2$	75.23	47.33	28.42	33.22 (CH)	23.87 (CH_3)
6e	5.35 (d, $J_{2,3}$ = 1.97 Hz, 1H)	C [c]	3.36 (m, 2H)	8.35 (br s, 3H, NH_3) 7.30-6.80 (m, 7H, Ar-H) 4.02 (q, 4H, 2 x OCH_2CH_3) 1.34 (t, 6H, 2 x OCH_2CH_3)	75.07	47.49	29.78	63.80 (OCH_2)	14.80 (CH_3)
6f	6.15 (s, 1H)	3.97 (m, 1H)	3.38 (m, 2H)	8.27 (br s, 3H, NH_3) 8.10-6.90 (m, 11H, Ar-H)	72.5	46.52	28.91		
6g	6.10 (s, 1H)	3.96 (m, 1H)	3.41 (m, 2H)	8.21 (br s, 2H, NH_3) 8.00-6.86 (m, 10H, Ar-H) 3.82 (s, 3H, OCH_3)	72.71	46.38	28.82	55.73 (OCH_3)	

[a] Hydrochloride salts. [b] In the free base, C-2H, appears as a sharp singlet at δ 5.10 (deuteriochloroform), even on 200 MHz instrument. [c] Could not be seen due to overlapping of other signals.

All glassware was thoroughly dried in an oven and cooled under dry nitrogen prior to use. THF was dried and distilled over lithium aluminum hydride and kept under dry nitrogen. Commercially available borane-THF complex (Aldrich) was used and transferred using oven-dried hypodermic syringes. Amine and hydroxylamine hydrochloride salts were prepared in a usual manner according to standard procedure [24] by bubbling anhydrous hydrogen chloride through a solution of the base in absolute ether. 3-Nitrochromenes were prepared *via* published procedures [7,8].

Synthesis of 3-Nitrochromans. General Procedure.

The synthesis of 2-(1-Naphthyl)-3-nitrodihydronaphtho[2,1-*b*]pyran, **4b**, is representative of the procedure employed. 2-(1-Naphthyl)-3-nitro-2*H*-naphtho[2,1-*b*]pyran, (**3b**, 2 mmoles, 0.706 g) was placed in an Erlenmeyer flask containing a magnetic stirring bar and dissolved in 110 ml of a mixed solvent system of tetrahydrofuran-methanol (10:1, v/v). Sodium borohydride (2.5 mmoles, 0.095 g) was then added, in four portions, to the well stirred solution by means of a spatula. A mildly exothermic reaction ensued with the gradual disappearance of the yellow coloration (nitrochromene). The mixture was stirred for 20 minutes at room temperature and then quenched with water (2 ml). The volatile solvents were removed under reduced pressure and water added (40 ml) and the aqueous suspension extracted with dichloromethane (4 x 30 ml). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. Recrystallization of the crude product from ether/tetrahydrofuran afforded **4b**, as colorless needles, 0.524 g (74%), mp 224-225°; ^{1}H nmr (deuteriochloroform): δ 3.84 (d, 2H, $J_{1,2}$ = 4 Hz, C-1H), 5.67 (m, 1H, C-2H), 6.13 (br s, 1H, C-3H), 8.1-7.2 (m, 13H, ArH); ^{13}C nmr (deuteriochloroform): δ 26.75 (C-1), 73.50 (C-3), 82.14 (C-2).

Anal. Calcd. for $C_{23}N_{17}NO_3$: C, 77.75; H, 4.79; N, 3.94. Found: C, 77.50; H, 5.06; N, 3.84.

2-Phenyl-3-nitrodihydronaphtho[2,1-*b*]pyran (**4a**).

2-Phenyl-3-nitro-2*H*-naphtho[2,1-*b*]pyran, **3a** (2 mmoles, 0.606 g) was reacted with sodium borohydride (2.5 mmoles, 0.095 g) as described in the general procedure. Recrystallization from ether afforded **4a**, 0.518 g (85%), mp 183-184°; ^{1}H nmr (deuteriochloroform): δ 3.67 (m, 2H, C-1H), 5.32 (m, 1H, C-2H), 5.47 (d, 1H, $J_{2,3}$ = 7.2 Hz, C-3H), 7.9-7.1 (m, 11H, Ar-H).

Anal. Calcd. for $C_{19}H_{15}NO_3$: C, 74.75; H, 4.92; N, 4.59. Found: C, 74.35; H, 5.13; N, 4.40.

Synthesis of 2-Arylsubstituted-3-Hydroxylaminochromans. General Procedure.

The synthesis of 2-phenyl-3-hydroxylamino-2*H*-1-benzopyran, **5a**, is representative of the procedure employed. A flame-dried, nitrogen-flushed, 250 ml flask, equipped with a septum inlet, magnetic stirring bar, and reflux condenser was cooled to 0°. Borane-THF complex (4 mmoles, 4.0 ml of a 1.0*M* solution) was injected into the reaction flask *via* a syringe, followed by the slow addition of a solution of 3-nitrochromene, **1a**, (2 mmoles, 0.506 g in 5 ml of THF). After the addition, the ice bath was removed and sodium borohydride (2 mmoles, 0.076 g) was added to the stirred reaction mixture by means of a spatula. A mildly exothermic reaction ensued. The reaction was allowed to proceed until the yellow color of the starting material disappeared (1 hour). The mixture was poured onto ice-water (40 ml) and acidified to *p*H 2 with 10% hydrochloric acid. The mixture was stirred, heated at 60-65° for 2 hours, and then cooled to room temperature. The acidic layer was extracted with ether (3 x 20 ml) and dried (magnesium sulfate). The solvent was removed under reduced pressure to afford a residue which upon recrystallization from ether/petroleum ether gave white needles 0.400 g (83%) of 2-phenyl-3-hydroxylamino-2*H*-1-benzopyran, mp 94-96°; ^{1}H nmr (deuteriochloroform): δ 2.98 (d, 2H, $J_{3,4}$ = 2.7 Hz, C-4H), 3.47 (m, 1H, C-3H), 5.24 (d, 1H, $J_{2,3}$ = 2.2 Hz, C-2H), 7.37-6.84 (m, 9H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 27.69 (C-4), 57.81 (C-3), 76.86 (C-2).

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.86; H, 6.45; N, 5.85.

Synthesis of 2-Arylsubstituted-3-aminochromans. General Procedure.

The synthesis of 2-phenyl-3-amino-2*H*-1-benzopyran, **6a**, is representative. A flame-dried, nitrogen-flushed, 250 ml flask equipped with a septum inlet, magnetic stirring bar, and reflux condenser was cooled to 0°. Borane-THF complex (8 mmoles, 8.0 ml of a 1.0*M* solution) was injected into the reaction flask *via* a syringe. This was followed by the slow addition of a solution of 3-nitrochromene (2 mmoles, 0.506 g in 5 ml of THF). After the addition, the ice bath was removed and sodium borohydride (1 mmole, 0.038 g) was added to the stirred reaction mixture by means of a spatula. A moderately exothermic reaction ensued. The reaction mixture was then heated at 65-70° overnight. After cooling to room temperature, the mixture was poured onto ice-water (40 ml), acidified to *p*H 2 and then stirred at 60-65° for 2 hours. After cooling to room temperature, the acidic layer was washed with ether (3 x 30 ml). The aqueous layer was basified with aqueous sodium hydroxide to ~*p*H 10, and extracted with ether (3 x 30 ml). The combined ethereal extracts were dried over anhydrous magnesium sulfate and the solvent-removed under reduced pressure to yield 0.400 g (89%) of 2-phenyl-3-amino-2*H*-1-benzopyran.

The hydrochloride salt was prepared by bubbling anhydrous hydrogen chloride into the ethereal solution (30 ml) and the product recrystallized from ethanol-ether, mp 261-263°; ^{1}H nmr (deuteriodimethylsulfoxide): δ 3.42 (m, 2H, C-4H), 4.0 (m, 1H, C-3H), 5.43 (d, 1H, $J_{2,3}$ = 1.54 Hz, C-2H), 7.61-6.92 (m, 9H, Ar-H), 8.33 (br s, 3H, NH_3); ^{13}C nmr (deuteriodimethylsulfoxide): δ 27.04 (C-4), 47.33 (C-3), 75.23 (C-2).

Anal. Calcd. for $C_{15}H_{16}ClNO$: C, 68.83; H, 5.73; N, 5.40. Found: C, 68.75, H, 6.01; N, 5.30.

Acknowledgement.

We wish to thank the Department of Energy (DE-FG05-86ER60434) for support of this research.

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