The 200-MHz $^1$H NMR and 25.034-MHz $^{13}$C spectra of the above material were essentially identical with the corresponding spectra of a sample prepared by acetylation of authentic (+)-*trans*-2,5-dimethylpyrrolidine.[7] A commercial mixture of *cis*- and *trans*-2,5-dimethylpyrrolidine was acetylated and examined by $^1$H and $^{13}$C NMR. The $^1$H NMR (200 MHz) showed a pair of doublets at $\delta$ 1.18 for the cis isomer.[13] The $^{13}$C NMR spectrum of the mixture shows the signals reported above for the trans isomer and, in addition, signals at $\delta$ 21.6, 22.2, 22.4, 31.1, 31.9, 53.5, and 54.8 for the cis isomer. The sample of **7a** prepared by cyclization of **6a** showed only trace signals attributable to the cis isomer in either the $^1$H or $^{13}$C spectra.

***N*-(Carbobenzoxy)-*trans*-2,5-dimethylpyrrolidine (7b).** The procedure described for **7a** was applied to 1.1 g (4.7 mmol) of **6b** in 80 mL of THF except that ether was used instead of methylene chloride for the back-extraction of the aqueous layers. Evaporative distillation (1.5 mm, 170 °C) gave 1.05 g (95% yield) of **7b**: IR (film) 1700 (C=O), 772 and 699 cm$^{-1}$ (Ph); $^1$H NMR (200 MHz) $\delta$ 1.08 (d, $J$ = 6.4 Hz, 3 H, $CH_3$), 1.18 (d, $J$ = 6.4 Hz, 3 H, $CH_3$), 1.4–1.7 (m, 2 H, 1 H on C-3 and on C-4), 2.0–2.2 (m, 2 H, 1 H on C-3 and C-4), 3.9–4.1 (m, 2 H, CHN), 5.08 (d, $J$ = 12 Hz, 1 H, $OCH_2$), 5.18 (d, $J$ = 12 Hz, 1 H, $OCH_2$) 7.35 (s, 5 H, aryl); $^{13}$C NMR (50.31 MHz) $\delta$ 19.4 and 20.6 ($2CH_3$), 29.4 and 30.3 (C-3 and C-4), 53.1 and 53.6 (C-2 and C-5), 66.3 ($OCH_2$), 127.76, 127.83, 128.4, and 137.4 (aryl), 154.2 (C=O).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00; O, 13.72. Found: C, 72.29; H, 8.30; N, 5.82; O, 13.59.

***N*-(Carbomethoxy)-*trans*-2,5-dimethylpyrrolidine (7c).** The procedure described for **7a** was applied to 790 mg (5.0 mmol) of **6c** except that ether was used for the back-extraction of the aqueous layers. Evaporative distillation (1.0 mm, 85 °C) gave 713 mg (90% yield) of **7c**: IR (film) 1694 (C=O); $^1$H NMR (90 MHz) $\delta$ 1.2 (overlapping doublets, 6H, $2CH_3$), 1.4–1.8 (m, 2 H, 1 H on C-3 and C-4), 1.8–2.3 (m, 2 H, 1 H on C-3 and C-4), 3.75 (s, 3 H, $OCH_3$), 3.8–4.2 (m, 2 H, C-2 and C-5 H); $^{13}$C NMR (25.034 MHz) $\delta$ 19.5 and 20.5 ($2CH_3$), 29.5 and 30.4 (C-3 and C-4), 51.8, 53.1, and 53.5 (C-2, C-5, and $OCH_3$), 155.0 (C=O).

***trans*-2,5-Dimethylpyrrolidine (3).** Glacial acetic acid (2 mL) containing HCl (~100 mg, 2.8 mmol) was added while stirring to distilled amide **7b** (632 mg, 2.7 mmol) and the mixture was stirred for 4 h. Then anhydrous HCl was passed over the surface while the mixture was stirred and heated gently overnight. To the resulting golden yellow solution, ~400 mL of dry ether was added. The white needlelike crystals of the amine hydrochloride were collected by filtration through a coarse glass frit funnel and dried under vacuum (crude weight 380 mg). Recrystallization from absolute EtOH/$Et_2O$ yielded a first crop of 252.4 mg (mp 184–185 °C) and a second crop of 40 mg (mp 179.5–183.5 °C) to give a total yield of 292.4 mg (80%). Repetitive recrystallization from absolute EtOH/$Et_2O$ gave material with a melting point of 185–186 °C (lit.[14] mp 187–188 °C): IR (KBr) 2400–3000 ($NH_2$), 1590 ($NH_2$) cm$^{-1}$; $^1$H NMR (200 Mhz) $\delta$ 2.54 (d, 6 H, $2CH_3$), 1.6–1.9 (m, 2 H, 1 H on C-3 and C-4), 2.1–2.4 (m, 2 H, 1 H on C-3 and C-4), 3.8–4.0 (m, 2 H, C-2 and C-5 H), 9.4–9.7 (b, 2 H, $^+NH_2$); $^{13}$C NMR (25.034 MHz) $\delta$ 18.0 ($2CH_3$), 32.2 (C-3 and C-4), 55.0 (C-2 and C-5).

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**Registry No. 3**, 39713-72-9; **5**, 59239-06-4; **6a**, 78329-34-7; **6b**, 78329-35-8; **6c**, 78329-36-9; **7a**, 57606-76-5; **7b**, 78329-37-0; **7c**, 78329-38-1; benzyloxycarbonyl chloride, 501-53-1; methyl chloroformate, 79-22-1.

# Condensation Products of 3-Halogenobenzanthrone Obtained by Using Fused Zinc Chloride. A New Convenient Method for Synthesizing Violanthrene B[1]

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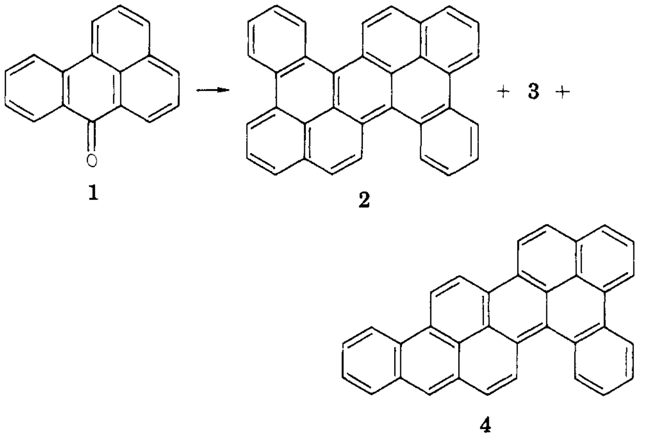
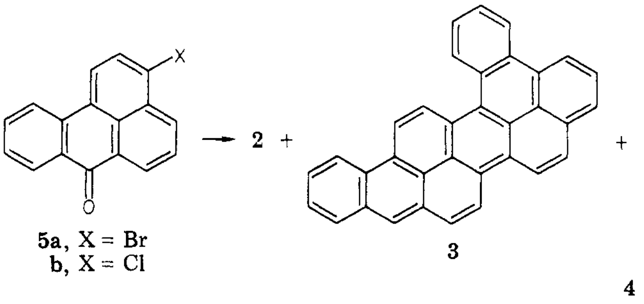
Previously we reported that benzanthrone (**1**) gave mainly tetrabenzo[*a*,*cd*,*j*,*lm*]perylene (**2**) and benzo[*rst*]phenanthro[1,10,9-*cde*]pentaphene (**4**) (isoviolanthrene B) and a small amount of dibenzo[*a*,*rst*]naphtho[8,1,2-*cde*]pentaphene (**3**) (violanthrene B) on heating with copper powder in a mixed flux of zinc chloride and sodium chloride.[2,3]



3-Bromobenzanthrone (**5a**) with similar treatment gave **3** in a good yield (38%) along with small amounts of **2** and **4**. 3-Chlorobenzanthrone (**5b**) furnished the same products in a similar ratio but in somewhat low yields.



This method provides a new and convenient synthesis of **3**, previously prepared by reduction of a byproduct (violanthrone B) formed in the violanthrone synthesis.[2,4]

## Experimental Section

**Condensation of 3-Bromobenzanthrone (5a).** In the mixed flux of 50 g of zinc chloride and 10 g of sodium chloride, 5.00 g of **5a** was maintained with 10.0 g of copper powder at 260 °C for

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(11) Wilson, S. R.; Sawicki, R. A. *J. Org. Chem.* **1979**, *44*, 330–336.

(12) Aido, T.; Legault, R.; Dugat, D.; Durst, T. *Tetrahedron Lett.* **1979**, 4993–4994.

(13) Differentiation of the cis and trans isomers of **7a** by $^1$H NMR was reported by House.[4] The appearance of the methyl doublets for the trans isomer is a function of the medium. The pure isomer shows a single doublet in deuteriochloroform but a pair of doublets in carbon tetrachloride.[4]

(14) Hill, R. K.; Chan, T.-H. *Tetrahedron* **1965**, *21*, 2015–2019.

(1) Part 4 of "Studies of Violanthrone B"; part 3, reference 2; part 2, J. Aoki, *Bull. Chem. Soc. Jpn.*, **34**, 1820 (1961).

(2) J. Aoki, M. Takekawa, S. Fujisawa, and S. Iwashima, *Bull. Chem. Soc. Jpn.*, **50**, 1017 (1977).

(3) In ref 2, 3 and 4 were shown by the convenient names dibenzo[*a*,*cd*]naphtho[3,2,1-*lm*]perylene (3) and dibenzo[*a*,*cd*]naphtho[1,2,3-*lm*]perylene (4), respectively.

(4) J. Aoki, *Bull. Chem. Soc. Jpn.*, **34**, 1817 (1961).

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1 h. Then the reaction mixture was treated with warm water containing a small amount of hydrochloric acid, and the insoluble part was collected, washed with water, and dried. The crude product (13.5 g) was refluxed with 600 g of chlorobenzene for 2 h, and the insoluble material was removed by hot filtration. The filtrate was evaporated to dryness, giving 3.00 g of brown solid. It was sublimated under vacuum ($10^{-3}$–$10^{-4}$ torr) at 150 °C and then 280–320 °C to give 0.486 g of recovered **5a** and 1.968 g of brown sublimates, respectively. The latter was recrystallized from chlorobenzene, giving 1.004 g of **3** which melted at 330–331 °C (lit.[2,4] orange-red needles, mp 331 °C, UV $\lambda_{max}$ ($C_6H_6$) 482 nm). The mother liquor was chromatographed on alumina and eluted with chlorobenzene. The products, obtained by evaporation of successive fractions, were purified by recrystallization and vacuum sublimation to give 66 mg of **2** (2%) (lit.[5] yellow needles, mp 331 °C, UV $\lambda_{max}$ ($C_6H_6$) 444 nm), 175 mg of **3** (total 1.179 g, 38%), 51 mg of recovered **5a** (total 537 mg, 10.7%), and 140 mg of **4** (4.5%) (lit.[2] brown-yellow needles, mp 307 °C, UV $\lambda_{max}$ ($C_6H_6$) 471 nm).

In addition, the use of zinc dust, instead of copper powder,[6] afforded comparable results to those described above when the reaction mixture was heated at 180–200 °C for 30 min.

**Condensation of 3-Chlorobenzanthrone (5b).** A mixture of 2.00 g of **5b**, 2.0 g of zinc dust,[7] 10 g of zinc chloride, and 2 g of sodium chloride was kept at 220–230 °C for 1 h, and the reaction mixture was worked up in a manner similar to that used for **5a**, giving 13 mg of **2** (1%), 333 mg of **3** (26%), 35 mg of **4** (2.7%), and 418 mg of recovered **5b** (20.9%).

**Acknowledgment.** We express our thanks to Professor Hiroo Inokuchi and Dr. Hidemasa Takaya of The Institute for Molecular Science for their kind advice.

**Registry No. 2**, 191-53-7; **3**, 191-46-8; **4**, 190-93-2; **5a**, 81-96-9; **5b**, 6409-44-5.

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[5] J. Aoki, *Bull. Chem. Soc. Jpn.*, **37**, 1079 (1964).

[6] The use of zinc dust is undesirable for 1 because of forming tarry matter.

[7] Copper powder was of little use to force this condensation reaction.

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# On the Mechanism of Imide Formation in the Thermolysis of $^{18}O$-Labeled *N*-Butylphthalamic Acid

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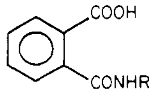
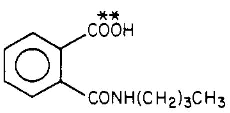
The thermal dehydration of phthalamic acids has long been a well-known method for the preparation of phthalimides;[1] however, the mechanism of imide formation in this reaction has not been elucidated. We have recently shown that the relative proportions of imide and anhydride obtained in thermolysis of a series of *N*-alkyl-substituted phthalamic acids **1** are very sensitive to the steric bulk of the alkyl residue on nitrogen.[2] Specifically, the amount of imide formed in the thermolysis of these compounds decreases dramatically with the number and size of branching groups on the carbon atom attached to nitrogen. Although there is evidence to suggest that isoimides are intermediates in the formation of imides,[3,4] we were unable to observe their formation in our study. We were able to show, however, that isoimides rearranged rapidly to imides under our conditions and thus the intermediacy of isoimides in the formation of imides remains a mechanistic possibility.



**1**

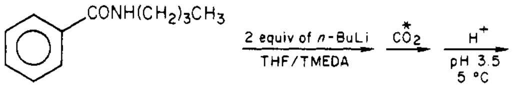


**2**

In evaluating the mechanistic implications of our observation of a steric inhibition to imide formation, we were interested in determining the "nucleophilic–electrophilic" relationship between the acid and amide functions in this ring closure reaction. In order to address this question experimentally, we have prepared the oxygen-18-labeled phthalamic acid **2** and examined by mass spectrometry the $^{18}O$ content of the phthalimide obtained from its thermolysis. The results of our examination are reported here.

## Results and Discussion

The $^{18}O$-labeled phthalamic acid **2** was chosen as a model compound because we had previously shown that *N*-*n*-butylphthalamic acid gives only imide upon thermolysis. Additionally, on the basis of an analysis of the mechanistic possibilities leading to imide formation, the labeled compound **2** might allow us to determine the "nucleophilic–electrophilic" relationship between the amide and acid functions in this ring closure reaction based on the $^{18}O$ content of the imide obtained from its thermolysis. The labeled phthalamic acid **2** was prepared by the ortho lithiation of *n*-butylbenzamide[5] and reaction of the resultant dianion with solid $CO_2$ (99.9% $^{18}O$) (eq 1). The oxygen–18 content of the phthalamic acid prepared in this manner was evaluated by field-desorption mass spectrometry.



(1)

This technique was chosen because other techniques such as electron impact result in rapid and complete conversion to imide. The field-desorption spectrum showed an isotopically uncomplicated ion cluster for the protonated molecule $(M + H)^+$ at *m*/*e* 226 completely consistent with clean incorporation of the labeled $CO_2$. Loss of label by exchange during the acid workup was therefore not observed. This point was further supported by our observation that unlabeled *N*-*n*-butylphthalamic acid failed to exchange its oxygens in $^{18}O$-enriched water (60% $^{18}O$) at pH 3 at 80 °C after 48 h. At pH values less than 3, oxygen scrambling was observed.

Heating in situ of the field-desorption emitter to about 200 °C resulted in imidization of the amic acid followed by observation of a molecular ion at *m*/*e* 205 for the product imide. The pattern observed for this ion was also isotopically uncomplicated, thereby indicating that imidization occurred exclusively with retention of a single $^{18}O$ label.

A second experiment involving imidization on the solids probe (200 °C) followed by analysis by electron-impact mass spectrometry provided an identical result. In both of these reactions the imidization reaction was solvent free

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