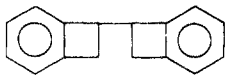
Reduction of 1 to the parent hydrocarbon could be effected by either Bu_3SnH or Bu_3SnCl–$LiAlH_4$.[13] This constitutes an efficient two-step synthesis of benzocyclobutene which compares favorably with other published methods.[14] Other transformations of 1 were less productive. NaN_3 (ethanol, 80 °C) converted 1 to a complex mixture of benzocyclobutenes which included the azide; the presence of the azide in the crude reaction mixture was confirmed by reduction to 1-aminobenzocyclobutene[9e] with $LiAlH_4$. Carbonation of the Grignard reagent derived from 1 afforded benzocyclobutenecarboxylic acid in low yield.[15] The principal neutral product, isolated as a pair of diastereomers, was tentatively identified as dimer 7. The



7

coupling reaction is not uncharacteristic of benzylic halides. Substance 7 was also obtained as the only detectable hydrocarbon product upon attempted alkylation of 1 with either CH_3MgBr or $(CH_3)_2CuLi$. Thus, although its reactivity is reduced somewhat relative to unstrained benzylic bromides, we expect 1 to enjoy renewed synthetic popularity, especially as it is now readily available via a one-pot reaction.

Experimental Section[16]

1-Bromobenzocyclobutene (1). A 250-mL flask, equipped with condenser, drying tower, and efficient magnetic stirrer, was charged with cycloheptatriene (freshly distilled, 27.6 g, 300 mmol), bromoform (freshly distilled, 25.3 g, 100 mmol), anhydrous K_2CO_3 (15.0 g, 109 mmol), and 18-crown-6 (0.75 g). The reaction vessel was immersed in an oil bath preheated to 145 °C. Progress of the reaction was monitored by regular VPC analysis. After ca. 10 h the reaction mixture was cooled, diluted with an equal volume of acetone, and treated with 10 g of silica gel. The insoluble solid residue was separated by suction filtration and the filter cake was washed with acetone until the washings were colorless. The liquid phases were combined and concentrated (rotary evaporator), and the residual cycloheptatriene was recovered by distillation at reduced pressure. The viscous, dark brown residue was added dropwise with stirring to 150 mL of hot petroleum ether (30–60). After filtration to remove precipitated solids, the solution was concentrated (rotary evaporator) and distilled in vacuo through a 15-cm Vigreaux column to afford 1 of >90% purity, contaminated only by 2. Pure 1 (4.78 g, 26%; 33% based on recovered bromoform) was obtained as a faintly yellow liquid by redistillation, bp 48–51 °C (0.75 mm) [lit.[4b] 55–59 °C (1 mm)]. It was stored at −15 °C until use.

1-Iodobenzocyclobutene (6b). A solution of 1 (1.83 g, 10.0 mmol) and NaI (4.5 g, 3 equiv) in 20 mL of acetone was heated at reflux for 12 h. The crude reaction mixture was concentrated and partitioned between water and ether. The organic layer was separated, washed with water and brine, and dried ($MgSO_4$). Solvent removal afforded the crude iodide as a nondistillable red liquid (2.05 g, 89% yield) free of NMR detectable impurities. The analytical sample was obtained by preparative TLC (hexane, R_f 0.45–0.65): ^1H NMR ($CDCl_3$) δ 3.6 (dd, J = 15 Hz, J' = 2 Hz, 1.0 H), 4.1 (dd, J = 15 Hz, J' = 4 Hz, 1.0 H), 5.7 (q, J = 4 Hz, J' = 2 Hz, 1.0 H), 7.1–7.6 (m, 4.0 H); mass spectrum, m/e (relative intensity) 230 (M^+, 2), 188 (3), 127 (4), 103 (M − I, 100), 91 (5), 63 (4), 51 (10).

Phosphonium Salt (6e). A mixture of 1 (1.83 g, 10.0 mmol) and triphenylphosphine (5.4 g, 2 equiv) was maintained at 110 °C in 10 mL of toluene for 48 h. The finely divided white solid which precipitated was collected and dried in vacuo (2.06 g, 46% yield), mp 218–222 °C dec, unchanged by recrystallization: ^1H NMR ($CDCl_3$) δ 3.0–3.6 (m, 2 H), 4.4–5.0 (m, 1 H), 7.0–8.5 (aromatics, 19 H). Anal. Calcd for $C_{26}H_{22}BrP$: C, 70.12; H, 4.98. Found: C, 70.16; H, 5.18.

Acknowledgment. Partial support of this work by the Horace H. Rackham School of Graduate Studies of the University of Michigan is gratefully acknowledged. We thank Mr. Vittorio J. Bruni for the preparation of **3a**.

Registry No. 1, 21120-91-2; **6b**, 78329-06-3; **6c**, 78329-07-4; 7 (isomer 1), 78329-08-5; 7 (isomer 2), 78329-09-6; cycloheptatriene, 544-25-2; bromoform, 75-25-2; benzocyclobutene, 694-87-1.

(13) Sanders, A.; Giering, W. P. *J. Org. Chem.* **1973**, *38*, 3005.
(14) Brewer, P. D.; Tagat J.; Hergrueter, C. A.; Helquist, P. *Tetrahedron Lett.* **1977**, 4573 and references therein.
(15) Horner et al.[3b] report isolation of the acid in 53% yield.
(16) Melting points are uncorrected. Routine NMR spectra were recorded on a Varian T-60 spectrometer in $CDCl_3$ solution with Me_4Si as an internal standard. Mass spectra were obtained with a Finnegan 4023 GC–MS instrument. Gas chromatography was performed on a Varian Aerograph 1720-5 gas chromatograph employing a 6 ft × $^1/_4$ in. 5% SF-96 column at 175 °C with He as the carrier gas.

Synthesis of *trans*-2,5-Dimethylpyrrolidine by Intramolecular Amidomercuration

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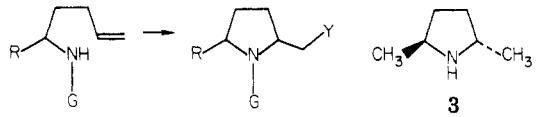
Received April 2, 1981

As part of another synthetic project, we became interested in the stereoselectivity of the electrophile-initiated cyclization of δ-alkenyl amine derivatives (1 → 2). In the



1 2 3

course of examining this question, we have developed an efficient, highly stereoselective synthesis of *trans*-2,5-dimethylpyrrolidine (3), a structure which has proven to be of interest as an easily resolved chiral amine containing a C_2 axis of symmetry.[1,3] The procedure described herein should also be applicable to the synthesis of other *trans*-dialkylpyrrolidines.[5,6]

The synthesis of 3 is outlined in Scheme I. The known conversion of the commercially available ketone 4 into oxime 5 proceeds in 88–97% yield.[4] Reduction of the oxime with lithium aluminum hydride and direct acylation of the crude product gave the amide derivatives 6 in 95–99% yields. Treatment with mercuric acetate in tetrahydrofuran followed by reduction with sodium borohydride gave the cyclization product 7 in yields of 90–98%. Careful examination of the product 7a by ^1H and ^{13}C NMR (XL-200) shows only trace signals for the cis isomer.[7]

(1) Whitesell, J. K.; Felman, S. W. *J. Org. Chem.* **1977**, *42*, 1663. Amine 3 was prepared through a procedure developed by P. Dervan[2] utilizing 2,5-hexanediol as starting material.
(2) Dervan, P. B.; Uyehara, T. *J. Am. Chem. Soc.* **1976**, *98*, 2003–2005.
(3) A mixture of *cis*- and *trans*-2,5-dimethylpyrrolidine is commercially available, but this mixture is not easily separated.[4]
(4) House, H. O.; Lee, L. F. *J. Org. Chem.* **1976**, *41*, 863–869.
(5) For another highly stereoselective approach to *trans*-2,5-dialkylpyrrolidines, see Macdonald, T. L. *J. Org. Chem.* **1980**, *45*, 193–94.
(6) *trans*-2,5-Dialkylpyrrolidines are characteristic components of the poison gland products of a variety of ant species: Pedder, D. J.; Fales, H. M.; Jaouni, T.; Blum, M; MacConnel, J.; Crew, R. M. *Tetrahedron* **1976**, 2275–2279; Jones, T. H.; Blum, M. S.; Fales, H. M. *Tetrahedron Lett.* **1979**, 1031–1034; Jones, T. H.; Frank, J. B.; Blum, M. S.; Fales, H. M. *Tetrahedron Lett.* **1980**, 789–792 and references cited therein.
(7) The proportion of cis isomer is estimated to be approximately 2% by comparison with a sample containing added cis isomer. Authentic 7a was prepared by acetylation of a sample of 3 kindly provided by J. Whitesell.[1] A mixture of 7a and the corresponding cis acetamide was prepared by acetylation of the commercially available mixture of *cis*- and *trans*-2,5-dimethylpyrrolidine.[3]

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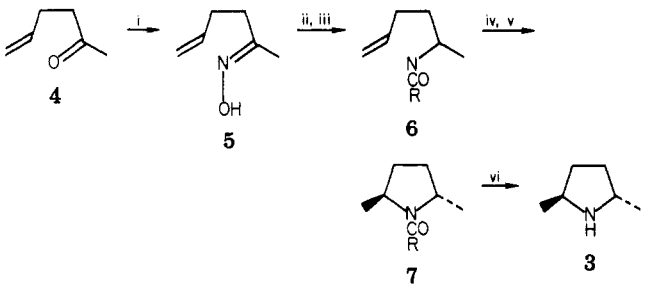
Scheme I[a]

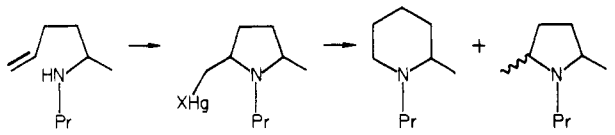


a, R = CH_3; b, R = $OCH_2C_6H_5$; c, R = OCH_3

[a] i, NH_2OH; ii, $LiAlH_4$; iii, RCOCl; iv, $Hg(OAc)_2$; v, $NaBH_4$; vi, HCl, HOAc.

Treatment of amide **7b** with HCl in acetic acid gave the hydrochloride of amine **3** in high yield. This synthesis of **3** proceeds in >70% overall yield and involves only four isolation steps with minimal purification.

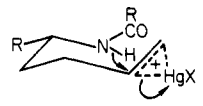
The cyclization step (**6** → **7**) is of interest both for its high yield and high stereoselectivity. The intramolecular aminomercuration of amine **8** has been reported[8] to give the pyrrolidine **9**, which upon sodium borohydride re-



8 **9** **10** **11**

duction gave, in 60% overall yield, a mixture of **10** and **11** with the pyrrolidine **11** apparently a mixture of cis and trans isomers. Our results indicate that amide derivatives react with greater regio- and stereoselectivity in this type of cyclization sequence.[9,10]

The stereochemistry of the cyclization of **6** → **7** is readily rationalized in terms of a preference for a chairlike transition state with an equatorial methyl group (**12**). Applications of this type of cyclization to more highly functionalized pyrrolidine derivatives are under investigation.



12

Experimental Section

General Procedures. Infrared spectra were determined on a Perkin-Elmer Model 297 or a Pye-Unicam Model SP3 infrared spectrophotometer. ^1H nuclear magnetic resonance spectra were obtained on Varian Associates Model T-60, EM-390, or XL-200 spectrometers. ^{13}C NMR spectra were obtained on JEOL PFT-100 (25.034 MHz) or Varian Associates XL-200 (50.31 MHz) spectrometers. All chemical shifts are reported as δ values in parts per million (ppm) relative to Me_4Si (δ Me_4Si = 0.00). Deuteriochloroform was used as the solvent for all NMR spectra.

All boiling points and melting points are uncorrected. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. The temperatures cited for these distillations refer to the maximum temperatures attained by the air oven during the distillation. Microanalyses were performed by Galbraith Laboratories, Inc.

2-(Acetylamino)-5-hexene (6a). A solution of oxime **5**[4] (5 g, 44 mmol) in ~50 mL of dry ether was added dropwise under nitrogen to a brine/ice chilled, magnetically stirred solution of lithium aluminum hydride (5.2 g, 137 mmol) in 600 mL of dry ether. The ice bath was removed and the stirred solution was allowed to warm to room temperature. The system was then equipped with a Friedrichs condenser and heated at reflux for 23 h under nitrogen. The flask was chilled in a brine/ice bath and the mixture was hydrolyzed by dropwise addition of 5 mL of H_2O, 5 mL of 15% NaOH, and then 15 mL of H_2O. The bath was removed and the solution was stirred overnight, treated with 20 g of a 1:1 mixture of $MgSO_4$ and Na_2SO_4, and stirred for an additional 11 h. Then 5 mL of acetic anhydride (5.4 g, 53 mmol) was added and the solution was stirred overnight. The resulting mixture was filtered and concentrated to a volume of ~100 mL. This solution was washed (bicarbonate, brine, and water), dried over $MgSO_4$, filtered, and concentrated. Distillation (95–102 °C, 1.0 mm) yielded 5.68 g and further evaporative distillation of the residue (0.9 mm, 100 °C) gave an additional 200 mg (total yield 5.88 g, 95% yield from oxime **5**) of 2-(acetylamino)-5-hexene (**6a**): IR (film) 3270 (NH), 1640 (C=O), 905 and 990 (CH=CH_2) cm^{-1}; ^1H NMR (90 MHz) δ 1.1 (d, J = 6.5 Hz, 3 H, $CHCH_3$), 1.2–1.8 (m, 2 H, CH_2), 1.9 (s, 3 H, CH_3CO), 1.8–2.3 (m, 2 H, allylic CH_2), 3.7–4.2 (m, 1 H, CHN), 4.7–5.2 (m, 2 H, CH=CH_2), 5.1–5.7 (br s, 1 H, NH) 5.4–6.1 (m, 1 H, CH=CH_2); ^{13}C NMR (25.034 MHz) δ 20.8 (C-1), 23.2 (CH_3CO), 30.4 and 35.9 (C-3 and C-4), 44.8 (C-2), 114.7 (C-6), 138.0 (C-5), 169.6 (C=O).

Anal. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92; O, 11.33. Found: C, 67.80; H, 10.63; N, 9.93; O, 11.64.

2-[(Carbobenzoxy)amino]-5-hexene (6b). The procedure described for preparation of **6a** was repeated with 2.5 g of oxime **5** and benzyloxycarbonyl chloride as the acylating agent to give, after microdistillation (5.0 g, bp 154–160 °C, 1.0 mm) and evaporative distillation of residue (130 mg, 1.8 mm, 130 °C), 5.13 g (99% yield) of carbamate **6b**: IR (film) 3315 (NH), 1695 (C=O), 910 and 990 (CH=CH_2), 694 and 734 (phenyl) cm^{-1}; ^1H NMR (90 MHz) δ 1.15 (d, J = 6.5 Hz, 3 H, CH_3), 1.3–1.7 (m, 2 H, CH_2), 1.9–2.3 (m, 2 H, allylic CH_2), 3.4–3.9 (m, 1 H, CHN), 4.2–4.8 (br s, 1 H, NH), 5.1 (s, 2 H, OCH_2Ph), 4.8–5.2 (m, 2H, CH=CH_2), 5.5–6.1 (m, 1 H, CH=CH_2), 7.3 (s, 5 H, Ph); ^{13}C NMR (25.034 MHz) δ 21.1 (C-1), 30.2 and 36.2 (C-3 and C-4), 46.8 (C-2), 66.4 (OCH_2), 114.8 (C=CH_2), 127.9, 128.2, and 136.6 (aryl), 137.8 (C-5), 155.7 (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, 72.13; H, 8.01; N, 5.90; O, 13.96.

2-[(Carbomethoxy)amino]-5-hexene (6c). The procedure described for preparation of **6a** was repeated with 2.5 g of oxime **5** and methyl chloroformate as the acylating agent to give, after microdistillation at 0.8 mm (bp 71–73 °C), 3.35 g (97% yield) of carbamate **6c**: IR (film) 3325 (NH), 1704 (C=O), 912 and 993 (CH=CH_2) cm^{-1}; ^1H NMR (90 MHz) δ 1.1 (d, J = 6.5 Hz, 3 H, CH_3), 1.3–1.7 (m, 2 H, CH_2), 1.9–2.3 (m, 2 H, allylic CH_2), 3.6 (s, 3 H, OCH_3), 3.5–4.0 (m, 1 H, CHN), 4.3–4.8 (br s, 1 H, NH), 4.8–5.3 (m, 2 H, HC=CH_2), 5.5–6.1 (m, 1 H, CH=CH_2); ^{13}C NMR (50.31 MHz) δ 21.2 (C-1), 30.2 and 36.2 (C-3 and C-4), 46.7 (C-2), 51.8 (OCH_3), 114.8 (=CH_2)), 137.9 (CH=CH_2), 156.4 (C=O).

***N*-Acetyl-*trans*-2,5-dimethylpyrrolidine (7a).** Mercuric acetate (2.6 g, 8.2 mmol) was added in one portion to a stirred solution of amide **6a** (770 mg, 5.4 mmol) in 60 mL of tetrahydrofuran. The mixture was purged with nitrogen, covered with aluminum foil, and stirred for 18 h. A solution of sodium borohydride (200 mg, 5.3 mmol) in 0.5 mL of 2.5 M NaOH was added dropwise to the mixture. The mixture was stirred overnight, treated with 3 mL of saturated Na_2CO_3, and stirred an additional 4 h. After the solution had been concentrated to remove tetrahydrofuran, the residue was diluted with ether and extracted with saturated carbonate (3×). The aqueous layers were combined and extracted with methylene chloride. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. Evaporative distillation (1.0 mm, 85 °C) gave 760 mg (98% yield) of **7a**: IR (film) 1630 cm^{-1} (C=O); ^1H NMR (200 MHz) δ 1.18 (d, J = 6.4 Hz, 6 H, $2CH_3$), 1.5–1.7 (m, 2 H, 1 H on C-3 and on C-4), 2.1 (s, 3 H, CH_3CO), 2.0–2.3 (m, 2 H, 1 H on C-3 and on C-4), 3.9–4.1 (m, 1 H, CHN), 4.1–4.3 (m, 1 H, CHN); ^{13}C NMR (25.034 MHz) δ 19.2 and 21.4 (CH_3), 22.8 (CH_3CO), 29.2 and 30.8 (C-3 and C-4), 52.9 and 54.3 (C-2 and C-5), 168.7 (C=O).

(8) Perie, J. J.; Laval, J. P.; Roussel, J.; Lattes, A. *Tetrahedron* **1972**, *28*, 675–699.

(9) Similar results have been noted by Clive in intramolecular aminoselenation reactions: Clive, D. L. J.; Farina, V.; Sing, A.; Wong, C. K.; Kiel, W. A.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2120–2126.

(10) Other examples of intramolecular amidomercuration which have been reported include a transannular cyclization[11] and a cyclization involving a β-lactam as the amide functionality.[12]

The 200-MHz ^1H 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 ^1H and ^{13}C NMR. The ^1H NMR (200 MHz) showed a pair of doublets at δ 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 δ 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 ^1H 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); ^1H NMR (200 MHz) δ 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) δ 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); ^1H NMR (90 MHz) δ 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) δ 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}; ^1H NMR (200 Mhz) δ 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) δ 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.

(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 ^1H 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.

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

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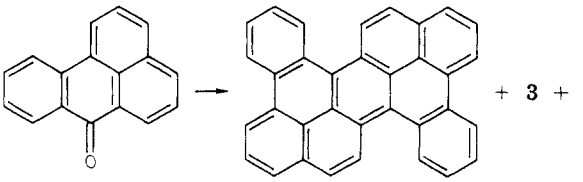
Received March 31, 1981

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]



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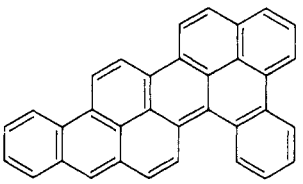
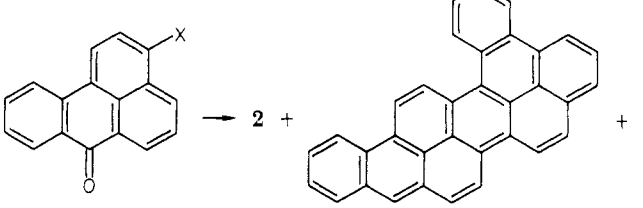


4

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.



5a, X = Br
b, X = Cl

3 4

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

(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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