After removal of the solvent under reduced pressure, the residue was purified on silica gel thin-layer chromatography to afford methyl benzoate (136 mg, 100%); MS, *m/z* 136 (M^+). This compound was identified with an authentic sample[19] by comparing their NMR and IR spectra.

Preparation of Thio Esters Using BTBO. A typical example is as follows: suspended BTBO (460 mg, 1 mmol) in acetonitrile (10 mL) was added to a solution of benzoic acid (122 mg, 1 mmol) and pyridine (79 mg, 1 mmol) in acetonitrile (10 mL). The reaction mixture became a clear solution in a second. After the reaction mixture was stirred for 1 h at room temperature, a solution of ethanethiol (69 mg, 1.1 mmol) and triethylamine (111 mg, 1.1 mmol) in acetonitrile (2 mL) was added at room temperature. Stirring was continued for an additional 5 h. The reaction mixture was quenched with water and product was extracted 3 times with ethyl acetate; then the combined ethyl acetate layer was successively washed with 4% $NaHCO_3$ solution, 1 H HCl solution, water, and brine, and dried over sodium sulfate. After removal of solvent under reduced pressure, the residue was separated by silica gel thin-layer chromatography to afford ethyl thiobenzoate: 154 mg (93%); MS, *m/z* 166 (M^+); IR (KBr) 1660 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (3 H, t, CH_3), 3.10 (2 H, q, CH_2), 7.33–8.02 (5 H, m, C_6H_5).

Registry No. 1, 26198-21-0; BTBO, 93605-83-5; Z-Ala-Ala-OEt, 5673-69-8; Z-Ala-Gly-OEt, 2503-32-4; Z-Phe-Gly-OEt, 2778-34-9; Z-Val-Gly-OEt, 2766-17-8; $PhCOOCH_3$, 93-58-3; $PhCH_2COOC_2H_5$, 101-97-3; $PhCH_2COOCH(CH_3)_2$, 4861-85-2; Z-Phe-OMe, 35909-92-3; $PhCOSC_2H_5$, 1484-17-9; $PhCH_2COSC_2H_5$, 14476-63-2; $PhCH_2COSC(CH_3)_3$, 61049-77-2; Z-Ala, 1142-20-7; Z-Phe, 1161-13-3; Z-Val, 1149-26-4; Ala-OEt·HCl, 1115-59-9; Gly-OEt, 459-73-4; 4-chloro-3-nitro-α,α,α-trifluorotoluene, 121-17-5; hydrazine, 302-01-2; oxalyl chloride, 79-37-8; benzoic acid, 65-85-0; benzeneacetic acid, 103-82-2.

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[19] The authentic samples were supplied from Aldrich Chemical Co.

Formation of Ethers from Ozonides by Reductive Cleavage of the Two C-O Bonds of the Peroxide Bridge

Tomohiro Fujisaka, Masatomo Nojima,* and
Shigekazu Kusabayashi

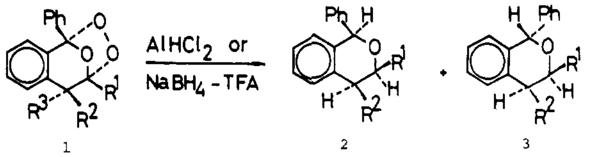
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received May 10, 1984

While developing a new transformation of ozonide (1,2,4-trioxolane),[1] it has been found that the reaction of *exo,endo*-1-methyl-3-phenyl- and *exo,endo*-1-methyl-2,3-diphenylidene ozonides **1e–h** with $AlHCl_2$ gives in each case a mixture of isomeric ethers (eq 1). Moreover, the product composition has been found to be a marked function of the stereochemistry of the ozonides.[1a] To obtain further insight into this novel transformation, we performed the reactions of a series of bicyclic and monocyclic ozonides (**1a–m**) with $AlHCl_2$ in diethyl ether[2] or with sodium borohydride in trifluoroacetic acid (TFA).[3]

Results and Discussion

Under the two reduction conditions, bicyclic ozonides **1a–j** were effectively reduced to give the corresponding ethers in 5–66% yield (Table I). Not only the stereochemistry of the bicylic ozonides **1a–h** but also the reduction conditions affected the stereochemistry of the product ethers.



(1)

1

a; R^1=Ph, R^2=R^3=H
b; R^1=Me, R^2=R^3=H
c; R^1=R^2=Ph, R^3=H
d; R^1=R^3=Ph, R^2=H
e; R^1=Ph, R^2=Me, R^3=H
f; R^1=Ph, R^2=H, R^3=Me
g; R^1=R^3=H, R^2=Me
h; R^1=R^2=H, R^3=Me
i; R^1=R^2=R^3=H

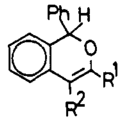
2

a; R^1=Ph, R^2=H
b; R^1=Me, R^2=H
c; R^1=R^2=Ph
d; R^1=Ph, R^2=Me
e; R^1=H, R^2=Me
f; R^1=R^2=H

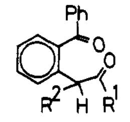
3

a; R^1=Ph, R^2=H
b; R^1=Me, R^2=H
c; R^1=R^2=Ph
d; R^1=Ph, R^2=Me
e; R^1=H, R^2=Me

Treatment of 2,3-diphenylindene ozonide (**1a**) with 8 molar equiv of $AlHCl_2$ in ether, gave together with diol **6a**, a mixture of *cis*-3,4-dihydro-1,3-diphenyl-1*H*-2-benzopyran (**2a**) and the trans isomer **3a** in 49% yield, the **2a**/**3a** ratio being 21:79. The reaction of **1a** in the system $NaBH_4$–TFA gave, however, a mixture of 73% **2a** and 27% **3a**.[4] The byproducts were diketone **5a** and 1,3-diphenyl-1*H*-2-benzopyran (**4a**). From *endo*-1-methyl-2,3-diphenylindene ozonide (**1f**) four isomeric ethers might have been formed. In reality, only two isomers, *cis,cis*- and *trans,cis*-3,4-dihydro-1,3-diphenyl-4-methyl-1*H*-2-benzopyrans (**2d**/**3d**), were produced. the trans, cis isomer **3d** was the major product in the reduction by $AlHCl_2$, whereas the reduction in the system $NaBH_4$–TFA gave predominantly the cis,cis isomer **2d**.

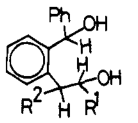


4a; R^1=Ph, R^2=H
4b; R^1=Me, R^2=H
4c; R^1=H, R^2=Me



5

a; R^1=Ph, R^2=H
b; R^1=Me, R^2=H
c; R^1=R^2=Ph
d; R^1=Ph, R^2=Me
e; R^1=H, R^2=Me



6

a; R^1=Ph, R^2=H
b; R^1=Me, R^2=H
c; R^1=Ph, R^2=Me
d; R^1=H, R^2=Me
e; R^1=R^2=H

The observed reagent-dependent product composition would be interpreted as follows (Scheme I). For $AlHCl_2$ reduction of **1f**, cleavage of the C–O bond of the peroxide bridge by $AlHCl_2$ would provide the carboxonium ion intermediate **13**. Since the $AlHCl_2$ coordinated to the peroxidic oxygen occupies a favorable position for hydride transfer, hydride transfer to **13** would occur predominantly from the same side as the methyl group to afford **14**. The absence of the cis,trans isomeric ether in the products would suggest that hydride transfer to **14** occurs exclusively from the less-hindered side. In the system $NaBH_4$–TFA, cleavage of the C–O bond leads to the formation of the carboxonium ion **15**. Attack by BH_4^- on **15** from the same direction as the methyl group is likely to be significantly prevented by the pseudoaxial methyl group. From **15**, therefore, the intermediate **16** is mainly produced, followed by hydride transfer from the less hindered side to yield the cis,cis ether **2d**.

In marked contrast to the case of endo ozonide **1f**, the compositions of the isomeric ethers from the exo isomer **1e** under two different conditions were almost reagent independent, cis,cis ether **2d** being obtained predominantly. A similar trend was also observed for *exo*-1,2,3-triphenylindene ozonide (**1c**). This preference of cis,cis ether **2d** clearly indicates that the transfer of the two

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(1) Miura, M.; Ikegami, A.; Nojima, M.; Kusabayashi, S.; McCulloug, K. J.; Nagase, S. *J. Am. Chem. Soc.* **1983**, *105*, 2414. (b) Yoshida, M.; Miura, M.; Nojima, M.; Kusabayashi, S. *Ibid.* **1983**, *105*, 6279. (c) Miura, M.; Nagase, S.; Nojima, M.; Kusabayashi, S. *J. Org. Chem.* **1983**, *48*, 2366.

(2) Eliel, E. L.; Nader, F. W. *J. Am. Chem. Soc.* **1970**, *92*, 3045. (b) Ashby, E. C.; Prather, J. *Ibid.* **1966**, *88*, 729.

(3) Gribble, G. W.; Leese, R. M. *Synthesis*, **1977**, 172.

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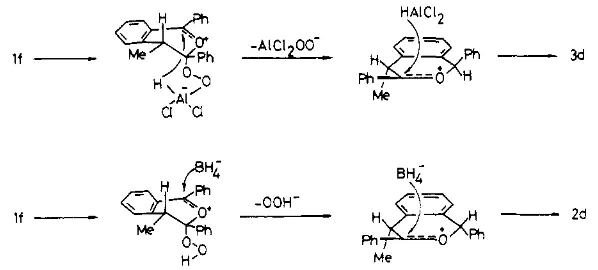
Table I. Hydrogenolysis of Ozonides

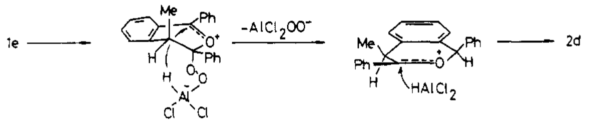
ozonide	condns[a]	ethers % yield	ethers 2/3 ratio	byproducts (% yield)
1a	A	49	21:79	**6a** (37)
1a	B	13	73:27	**4a** (15), **5a** (42)
1b	A	17	48:52	**4b** (3), **6b** (6)
1b	B	21	61:39	**5b** (12)
1c	A	43	76:24	
1c	B	5	78:22	**5c** (23)
1d	A	40	26:74	
1e	A[b]	66	88:12	**6c** (10)
1e	B	30	82:18	**5d** (35)
1f	A[b]	44	20:80	**6c** (15)
1f	B	40	80:20	**5d** (35)
1g	A[b]	42	95:5	**4c** (25), **6d** (30)
1g	B	36	62:38	
1h	A[b]	18	40:60	**6d** (30)
1h	B	31	79:21	**5e** (9)
1i	A	39		**6e** (12)
1i	B	30		
1j	A	18		**7** (27)
1j	B	36		**6g** (8)
1k	A			**8** (26), **10a** (7), **12** (17)
1k	B	27		**8** (4)
1l	B	31[c]		**8** (1), **10b** (2), **11** (10), **12** (6)
1m	A			**9** (39)
1m	B	33		**10b** (15)

[a] Condition A: Treatment of ozonide with 8 molar equiv of $AlHCl_2$ (prepared by mixing $LiAlH_4$ and 3 molar equiv of $AlCl_3$) in ether at 20 °C for around 1 h. Condition B: A CH_2Cl_2 solution of ozonide (3 mmol) was treated with a mixture of $NaBH_4$ (15 mmol) and TFA (25 mL). [b] Taken from the data in ref 1a. [c] A mixture of **2h**, **2i**, and **2j** was obtained in yields of 6%, 10%, and 15%, respectively.

Scheme I

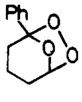


Scheme II

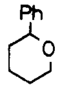


hydride ions occurs predominantly from the side opposite to the methyl group, suggesting that the steric bulk of the methyl substituent controls the course of the reaction (Scheme II).

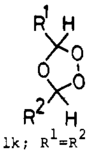
Reduction of monocyclic ozonides **1k** and **1m** in the system $NaBH_4$–TFA yielded the expected ethers **2h** and **2j**, respectively. In the case of $AlHCl_2$ reduction, however, the ethers were not obtained. Surprisingly, the reaction of 1-phenylheptene ozonide (**1l**)[5] in the $NaBH_4$–TFA



1j



2g



1k; $R^1=R^2=Ph$

1l; $R^1=Ph$, $R^2=$pentyl

1m; $R^1=R^2=$pentyl

$R^1CH_2OCH_2R^2$

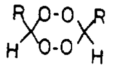
2h; $R^1=R^2=Ph$

2i; $R^1=Ph$, $R^2=$pentyl

2j; $R^1=R^2=$pentyl

$PhCH(OH)CH_2CH_2CH_2CH_2OH$

6g



10a; R=Ph

10b; R=pentyl

$PhCH=CHCH_2CH_2CH_2OH$

7

$PhCH_2OH$ 8

$Me(CH_2)_5OH$ 9

PhCHO 11

PhOH 12

system gave a mixture of benzyl ether (**2h**), hexyl ether (**2j**), and benzyl hexyl ether **2i**. The reason is obscure.

Experimental Section

Reaction of 2,3-Diphenylidene Ozonide (1a) with $AlHCl_2$. To anhydrous $AlCl_3$ (12 mmol) was added anhydrous ether (40 mL) at 0 °C, followed by 4 mmol of $LiAlH_4$. To this solution was added a solution of **1a** (2 mmol) in ether (40 mL) in 5 min. The mixture was kept at 0 °C for 15 min, and then the reaction was continued at 20 °C for 45 min. The products were column chromatographed on silica gel. Elution with petroleum ether–benzene (7:3) gave *trans*-3,4-dihydro-1,3-diphenyl-1*H*-2-benzopyran (**3a**) in 39% yield: mp 110–110 °C (from methanol); MS, *m/e* 286 (M^+); ^1H NMR δ 3.09 (d, J = 7.0 Hz, 2 H), 4.79 (t, J = 7.0 Hz, 1 H), 6.04 (s, 1 H), 7.08–7.40 (m, 14 H). Anal. Calcd for $C_{21}H_{18}O$: C, 88.10; H, 6.30. Found: C, 87.78; H, 6.37. From the second fraction was obtained the cis isomer **2a**: mp 108–110 °C (from methanol); ^1H NMR δ 2.97 (d × d, J = 4.0 and 16.0 Hz, 1 H), 3.24 (d × d, J = 10.0 and 16.0 Hz, 1 H), 4.95 (d × d, J = 4.0 and 10.0 Hz, 1 H), 5.91 (s, 1 H), 7.12–7.52 (m, 14 H). On the basis of Kalplus theory, the pseudoequatorial hydrogen signal of **3a** at the 1-position was presumed to appear at a lower field compared with the pseudoaxial hydrogen of **2a** at the same position. Consistent with this assignment, the hydrogenation of 1,3-diphenyl-1*H*-2-benzopyran (**4a**) over 10% palladium on charcoal gave predominantly the cis ether **2a**. Elution with ether gave diol **6a** in 37% yield: an oil; IR 3350, 1025 cm^{-1}.

Reaction of 1-Phenylheptene Ozonide (1l) in the System $NaBH_4$–Trifluoroacetic Acid. In a 50-mL flask, equipped with a magnetic stirrer and maintained under N_2, was added TFA (25 mL). $NaBH_4$ (15 mmol) was added in 15 min at 0 °C, followed by addition of a CH_2Cl_2 solution (15 mL) of 11 (3 mmol) at this temperature in 15 min. Then the reaction was continued at 20 °C for 30 min. Column chromatography on silica gel (elution with petroleum ether–benzene) afforded first hexyl ether (**2j**): an oil MS, *m/e* 186 (M^+); ^1H NMR δ 0.89 (t, J = 5.0 Hz, 6 H), 1.16–1.66 (m, 16 H), 3.28 (t, J = 6.0 Hz, 4 H). From the second fraction was obtained benzyl hexyl ether (**2i**): an oil; MS, *m/e* 192 (M^+); ^1H NMR δ 0.89 (t, J = 5.0 Hz, 3 H), 1.18–1.68 (m, 8 H), 3.34 (t, J = 6.0 Hz, 2 H), 4.38 (s, 2 H), 7.10–7.30 (m, 5 H). The third fraction contained benzyl ether (**2h**): an oil; MS, *m/e* 198 (M^+);

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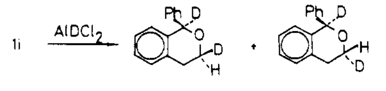
(4) The reaction of 2-methyl-3-phenylindene ozonide (**1b**) with $AlHCl_2$, however, exerted a poor stereoselectivity. The reaction of **1i** with AlDCl2 also gave two isomeric products in exactly equal amounts (eq 2). The reason for this lack of stereoselectivity is obscure.



(2)

(5) Miura, M.; Nojima, M. *J. Am. Chem. Soc.* **1980**, *102*, 288. May be in harmony with this, the reaction of **11** with catalytic amounts of $SbCl_5$ in methylene chloride affords a mixture of 3,6-diphenyl-, 3,6-dipentyl-, and 3-phenyl-6-pentyl-1,2,4,5-tetroxanes.

^{1}H NMR δ 4.50 (s, 4 H), 7.30 (s, 10 H). Elution with ether gave benzyl alcohol.

Physical Properties of Product Ethers. The ether **2c** was a solid: mp 148–150 °C (from methanol); MS, *m/e* 362 (M^+); ^{1}H NMR δ 4.29 (d, *J* = 4.0 Hz, 1 H), 5.37 (d, *J* = 4.0 Hz, 1 H), 6.00 (s, 1 H). Anal. Calcd for $C_{27}H_{22}O$: C, 89.50; H, 6.10. Found: C, 88.65; H, 6.08. **3c**: mp 202–203 °C (from methanol); ^{1}H NMR δ 4.14 (d, *J* = 4.0 Hz, 1 H), 5.15 (d, *J* = 4.0 Hz, 1 H), 6.34 (s, 1 H). Anal. Calcd for $C_{27}H_{22}O$: C, 89.50; H, 6.10. Found: C, 88.81; H, 6.13. **2f**: mp 87–89 °C (from methanol); ^{1}H NMR δ 2.55–3.26 (m, 2 H), 3.66–4.66 (m, 2 H), 5.67 (s, 1 H), 6.65–7.38 (m, 9 H); IR 1490, 1450, 1280 cm^{-1}. **2g**: an oil; ^{1}H NMR δ 1.24–1.88 (m, 6 H), 3.30–3.56 (m, 1 H), 3.94–4.23 (m, 2 H), 7.20 (m, 5 H). **4a**: mp 115–116 °C (from methanol); MS, *m/e* 284 (M^+); ^{1}H NMR δ 6.26 (s, 1 H), 6.48 (s, 1 H), 7.08–7.80 (m, 14 H); IR 1630, 1490, 1450 cm^{-1}. **4b**: an oil; ^{1}H NMR δ 1.92 (s, 3 H), 5.67 (s, 1 H), 6.07 (s, 1 H), 6.88–7.80 (m, 9 H).

The physical properties of **2d**, **2e**, **3d**, **3e**, and **6c** have been described previously.[1a] The ethers **2b** and **3b** were not obtained in pure states.

Registry No. **1a**, 91859-82-4; **1b**, 93645-80-8; **1c**, 89619-51-2; **1d**, 89675-06-9; **1e**, 84810-15-1; **1f**, 84847-61-0; **1g**, 84810-14-0; **1h**, 84847-60-9; **1i**, 73258-06-7; **1j**, 93645-81-9; **1k**, 23888-15-5; **1l**, 72328-17-7; **1m**, 72328-16-6; **2a**, 93645-82-0; **2b**, 93645-83-1; **2c**, 93645-84-2; **2d**, 84810-30-0; **2e**, 84810-47-9; **2f**, 2292-59-3; **2g**, 4203-44-5; **2h**, 103-50-4; **2i**, 61103-84-2; **2j**, 112-58-3; **3a**, 93645-85-3; **3b**, 93645-86-4; **3c**, 93645-87-5; **3d**, 84810-36-6; **3e**, 84810-46-8; **4a**, 93645-88-6; **4b**, 93645-89-7; **4c**, 50431-53-3; **5a**, 53067-91-7; **5b**, 93645-90-0; **5c**, 50805-40-8; **5d**, 75519-83-4; **5e**, 84810-25-3; **6a**, 93645-91-1; **6b**, 93645-92-2; **6c**, 93645-93-3; **6d**, 93645-94-4; **6e**, 22440-32-0; **6g**, 1011-61-6; **7**, 37464-86-1; **8**, 100-51-6; **9**, 111-27-3; **10a**, 16204-37-8; **10b**, 93645-95-5; **11**, 100-52-7; **12**, 108-95-2; $AlCl_2H$, 13497-97-7; $LiAlH_4$, 16853-85-3; $AlCl_3$, 7446-70-0.

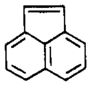
Aceanthrylene

Hans-Dieter Becker,* Lars Hansen, and Kjell Andersson

Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg, Sweden

Received June 26, 1984

There is an abundance of reports dealing with the chemistry of acenaphthylene (**1**), but nothing is known about the properties of its benzo derivative aceanthrylene (**2**) which, according to *Chemical Abstracts* nomenclature,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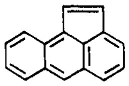
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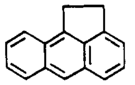

3

is the parent compound of a hydrocarbon ring system.[1,2] As a nonalternant conjugated, peri-condensed polycyclic hydrocarbon, aceanthrylene has been of interest in the context of molecular orbital calculations,[3] but the compound itself, remarkably, has never been available or described.[4] By contrast, the synthesis of its dihydro derivative, aceanthrene (**3**), first attempted in 1911 by Liebermann and Zsuffa, was successfully carried out by Fieser and Peters in 1932 and subsequently improved by Bergmann and Ikan (1958).[5-7]

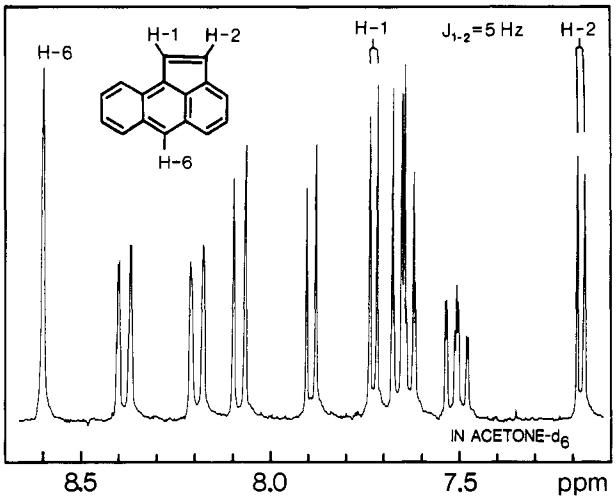
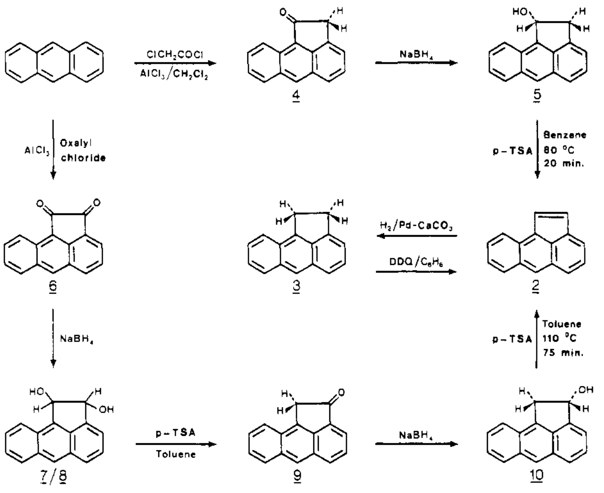


Figure 1. ^{1}H NMR spectrum (270 MHz) of aceanthrylene in acetone-d_6.

Scheme I



In conjunction with previous and current studies on the relationship between molecular geometry and photochemical properties of anthracenes,[8] we were enticed to prepare aceanthrylene. Its synthesis was accomplished by the following straightforward routes summarized in Scheme I.

Friedel–Crafts acylation of anthracene with chloroacetyl chloride in the presence of aluminum chloride (molar ratio

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(1) A summary of references dealing with the chemistry of acenaphthylene can be found in *Beilstein* **1980**, *EIV 5*, 2138 and corresponding preceding volumes.

(2) Besides benzo[*a*]fluoranthene (cf. Ray, J. K.; Harvey, R. G. *J. Org. Chem.* **1982**, *47*, 3335), at least two examples of substituted aceanthrylenes are known, namely, the 1-methyl-2-chloromethyl derivative (Hauptmann, S.; Franke, L.; Dietrich, K.; Wild, G.; Schnitzker, M. *Z. Chem.* **1963**, , 147) and 1,2-dimethylaceanthrylene (Kikuchi, H.; Seki, S.; Yamamoto, G.; Mitsuhashi, T.; Nakamura, N.; Oki, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1514).

(3) (a) Zahradnik, R.; Michl, J.; Koutecky, J. *Collect. Czech. Chem. Commun.* **1964**, *29*, 1932. (b) DasGupta, A.; DasGupta, N. K. *Can. J. Chem.* **1976**, *54*, 3227.

(4) After this paper had been submitted, the synthesis of aceanthrylene from 2-aceanthrenol was reported: Plummer, B. F.; Al-Saigh, Z. Y.; Arfan, M. *J. Org. Chem.* **1984**, *49*, 2069. The melting point reported for 2-aceanthrenol (228–230 °C) differs significantly from that found in the present work (209–210 °C), but we have no reason to doubt the purity of our 2-aceanthrenol. The melting point of aceanthrylene reported previously is 95–96 °C, while we find a melting point of 103–104 °C. Moreover, aceanthrylene has been reported to exhibit anomalous fluorescence, i.e., second excited state emission (Plummer, B. F.; Al-Saigh, Z. Y.; Arfan, M. *Chem. Phys. Lett.* **1984**, *104*, 389). However, aceanthrylene of the present work was found to be nonfluorescent. Consequently, we believe aceanthrylene of the present work to be emission spectroscopically pure, and its electronic absorption spectrum as shown in Figure 2 to be correct.

(5) Liebermann, C.; Zsuffa, M. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 852.

(6) Fieser, L. F.; Peters, M. A. *J. Am. Chem. Soc.* **1932**, *54*, 4373.

(7) Bergmann, E. D.; Ikan, R. *J. Org. Chem.* **1958**, *23*, 907. For other references dealing with aceanthrene, see: *Beilstein* **1965**, *EIII 5*, 2235.

(8) Becker, H.-D. *Pure Appl. Chem.* **1982**, *54*, 1589. Becker, H.-D.; Andersson, K. *J. Org. Chem.* **1983**, *48*, 4542 and references cited therein.

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