Rearrangements and Ring Expansions of 4*H*-Cyclopenta[*def*]phenanthrene Derivatives

Takao Kimura, Masahiro Minabe,* and Kazuo Suzuki

Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321-31, Japan

Received July 12, 1977

4*H*-Cyclopenta[*def*]phenanthrene (**1**)[1] is of interest because it is a strained molecule combining special features of both the fluorene and the phenanthrene structures, but the reactivities of **1** have been scarcely reported.[2]

The present paper deals with rearrangements and ring expansions on the active methylene bridge of **1**.

Pyrene (**2**) and its homologues were synthesized in good yields by Wagner–Meerwein rearrangements of the corresponding alcohols, which were obtained through the series of reactions indicated below. Alcohols **3** and **4** were converted into **5**[3] and **6**[4] without the formation of cyclopropane and vinyl by-products.

$$1 \longrightarrow 7 \longrightarrow 8 \longrightarrow 9 \longrightarrow 2;\ 7 \longrightarrow 13 \longrightarrow 14 \longrightarrow 3 \longrightarrow 5$$
$$10 \qquad\quad 11 \qquad\quad 1 \longrightarrow 15 \longrightarrow 16 \longrightarrow 4 \longrightarrow 6$$
$$12$$

Heterocyclic compounds **17**,[5] **18**,[6] and **19**[5] were obtained by methods similar to those employed in fluorene derivatives as follows.

$$1 \rightarrow 20 \rightarrow 21 \rightarrow 17;\ 20 \rightarrow 18;\ 20 \rightarrow 22 \rightarrow 19$$

The IR and NMR spectra of lactam **17** showed that there was no detectable amount of the enol form.

3,4-Benzocoumarin[7] was cleaved to 2′-hydroxydiphenyl-2-carboxylic acid under the basic conditions; however, the same scission in lactone **18** did not occur. This suggests that two groups, 4-COONa and 5-ONa, at the phenanthrene skeleton are large enough to prevent their existence in the same plane.

Pinacol **23** was changed into pinacolone **24** by pinacolic rearrangement, which was in turn converted into fluorescent hydrocarbon **25** through retro-pinacol rearrangement of its reduction product **26**. The scission of spiro carbon and carbonyl carbon atoms in **24** was resisted under the same basic conditions which resulted in the formation of 2′-(9-fluorenyl)diphenyl-2-carboxylic acid from 10-(2,2′-biphenylylene)-9-phenanthrone.[8] This finding can be ascribed to cause a similar reaction to that cited for **18** vs. 3,4-benzocoumarin.

The Wolff–Kishner reduction of **24** was attempted under the ordinary conditions and gave alcohol **26** but not the expected hydrocarbon. Actually, **24** could not form hydrazone derivatives. It is therefore evident that hydrazine hydrate behaves simply as a reductant in regard to **24**.

Experimental Section

All the melting points are uncorrected. All the new compounds gave correct elemental analyses. The instruments used in these analyses have been described elsewhere.[9]

4,5-Phenanthryleneacetic Acid (7).[1] A solution of 1.9 g (10 mmol) of **1** in 25 mL of xylene was added dropwise to an *n*-BuLi solution prepared from 2.0 g (15 mmol) of *n*-BuBr; crushed dry ice (ca. 5.0 g) was added gradually to the mixture at −10 °C. The resulting mixture was refluxed for 1 h to afford 1.30 g (56%) of **7**, mp 250–251 °C (dec). Methyl ester (**13**),[10] mp 63.5–64.5 °C. Ethyl ester (**8**): mp 51.5–53.0 °C; IR 1730 cm^{-1}; NMR (CCl_4) δ 1.25 (3 H, t, J = 6.0 Hz), 4.17 (2 H, q), 5.19 (1 H, s), and 7.30–8.03 (8 H, m).

When the reaction was carried out using 6.0 g (44 mmol) of *n*-BuBr, 5-(4,5-phenanthrylene)nonane (**10**) was obtained in 1.45-g (48%) yield: mp 88.5–89.5 °C; mass spectrum *m/e* 302 (M^+), 245, and 203.

4-Acetylcyclopenta[*def*]phenanthrene (15). This compound was prepared by the reaction[11] of **1** with EtOAc in 48% yield: mp 89–91 °C; NMR (CCl_4) δ 1.66 (3 H, s), 5.14 (1 H, s), and 7.45–8.00 (8 H, m).

Methyl 2-(4,5-Phenanthrylene)propionate (14) and 4-Methyl-4-acetylcyclopenta[*def*]phenanthrene (16). Ester **13** (1.00 g, 4 mmol) was dissolved in MeOH containing NaOMe (0.38 g or 0.0165 g-atom of Na in 25 mL of MeOH); then the mixture was stirred with 4.56 g (32 mmol) of MeI for 24 h at room temperature to yield 0.93 g (89%) of **14**: mp 108.0–109.5 °C; IR 1722 cm^{-1}; mass spectrum *m/e* 262 (M^+); NMR (CCl_4) δ 1.88 (3 H, s), 3.52 (3 H, s), and 7.52–8.10 (8 H, m).

Compound **16** was obtained in 94% yield: mp 99–100 °C; IR 1698 cm^{-1}; mass spectrum *m/e* 246 (M^+), 203, 202, and 189; NMR (CCl_4) δ 1.37 (3 H, s), 1.73 (3 H, s), and 7.45–7.94 (8 H, m).

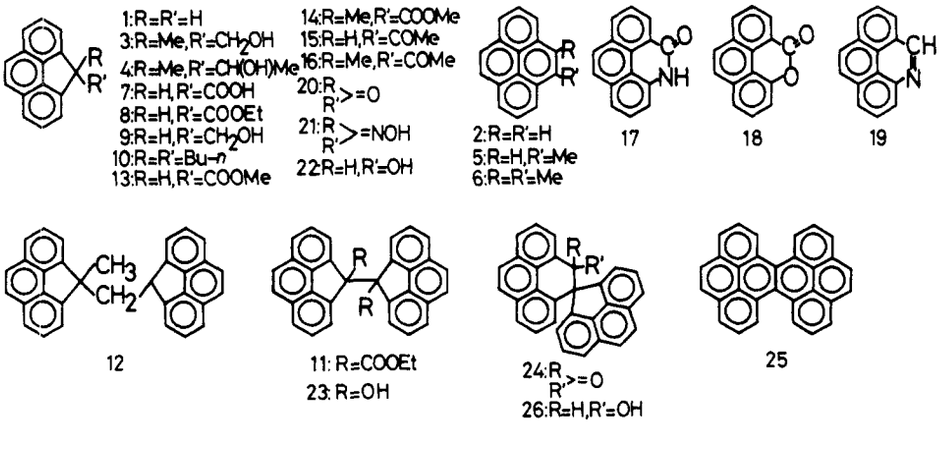
2-(4,5-Phenanthrylene)ethanol (9) and its Homologues. To a suspension of $LiAlH_4$ (0.10 g, 2.6 mmol) in 20 mL of ether was added dropwise 1.00 g (3.8 mmol) of **8** in 20 mL of ether with stirring over 30 min. The mixture was stirred for 1 h at room temperature and refluxed over an additional 30 min to yield, after workup, 0.40 g (48%) of **9**: mp 159–160 °C; IR 3210 and 3120 cm^{-1}; mass spectrum *m/e* 220 (M^+); NMR (C_6D_6) δ 3.68 (2 H, d, J = 7.2 Hz), 4.34 (1 H, t), 7.19 (1 H, s), and 7.43–8.07 (8 H, m). In addition, 0.06 g (6%) of ethyl 1,2-di(4,5-phenanthrylene)succinate (**11**) was isolated, mp 226–227 °C; IR 1721 cm^{-1}; NMR (C_6D_6) δ 0.79 (6 H, t, J = 7.2 Hz), 4.03 (4 H, q), and 7.03–7.80 (16 H, m).

The reduction was done using 1.44 g (38 mmol) of $LiAlH_4$ to afford 0.18 g (23%) of 1,3-di(4,5-phenanthrylene)butane (**12**): mp 175.5–177.0 °C; mass spectrum *m/e* 406 (M^+), 217, 203, and 189; NMR (C_6D_6) δ 1.55 (3 H, s), 2.74 (2 H, d, J = 4.5 Hz), 3.55 (1 H, t), and 6.55–7.74 (16 H, m).

2-(4,5-Phenanthrylene)propanol (**3**) was prepared from **14** in 84% yield: mp 108–109 °C; IR 3275 cm^{-1}; mass spectrum *m/e* 234 (M^+); NMR (C_6D_6) δ 1.39 (1 H, s), 1.55 (3 H, s), 3.57 (2 H, s), and 7.23–7.97 (8 H, m).

3-(4,5-Phenanthrylene)-2-butanol (**4**) was obtained from **16** in 50% yield: bp 203–207 °C (2 Torr, uncorrected); IR 3570 and 3420 cm^{-1}; mass spectrum *m/e* 248 (M^+), 204, 202, and 189; NMR (CCl_4) δ 0.61 (3 H, d, J = 6.3 Hz), 1.57 (3 H, s), 1.70 (1 H, s), 4.12 (1 H, q), and 7.32–7.93 (8 H, m).

Wagner–Meerwein Rearrangements of Alcohols 3, 4, and 9.



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A mixture of **9** (0.25 g, 1.1 mmol) and P_2O_5 (0.50 g) in xylene (20 mL) was refluxed for 2 h to give 0.22 g (95%) of **2**, which was identical in all respects with an authentic specimen.

By the same method, **3** was converted into 4-methylpyrene (**5**) in 82% yield, mp 147.5–148.5 °C.

4,5-Dimethylpyrene (**6**) was produced from **4** in 85% yield, mp 215–216 °C.

Beckmann Rearrangement of 4-Hydroxyiminocyclopenta[*def*]phenanthrene (21). A mixture of **21**[5] (1.095 g, 5 mmol, prepared from **20**[1] in 96% yield) and PPA (80%, 30 g) was stirred at 175–180 °C for 5 min to yield 0.62 g (57%) of 4,5-dihydro-4-azapyren-5-one (**17**): mp 348–350 °C (dec); IR 3160 and 1661 cm^{-1}.

Reaction of 4-Oxocyclopenta[*def*]phenanthrene (20) with Hydrogen Peroxide. To a solution of **20** (0.51 g, 2.5 mmol) in HOAc (30 mL) were added dropwise concentrated H_2SO_4 (7 mL) and then H_2O_2 (28%, 2.5 mL). The mixture was stirred at room temperature for 2 h to afford 0.45 g (82%) of 4-oxapyren-5-one (**18**): mp 200.5–201.5 °C; IR 1727 cm^{-1}.

4-Azapyrene (19). Concentrated H_2SO_4 (2 mL) was added to a suspension of NaN_3 (0.57 g, 8.8 mmol) in $CHCl_3$ (5 mL) at −10 °C with stirring for 30 min; then a suspension of 4-hydroxycyclopenta[*def*]-phenanthrene (**22**)[12] (1.03 g, 5 mmol, prepared from **20** in 86% yield) in $CHCl_3$ (50 mL) was added to the first mixture at 25 °C during a period of 20 min. After stirring at room temperature for an additional 1 h, ice (20 g) was added and the resulting mixture was allowed to stand overnight; **19** (0.43 g, 43%), mp 157.5–159.0 °C, was isolated.

Di(4,5-phenanthrylene)-1,2-ethanediol (23). Ketone **20** (2.04 g, 10 mmol) was treated with $TiCl_4$ (3.0 g, 15.8 mmol) and Zn dust (1.96 g, 0.03 g-atom) in THF (140 mL) according to the method described elsewhere[9] to give 1.73 g (84%) of **23:** mp 230.5–232.0 °C (dec); IR 3525 cm^{-1}; NMR (Me_2SO-d_6) δ 3.40 (2 H, s) and 6.25–8.05 (16 H, m).

Pinacol–Pinacolone Rearrangement of 23. A solution of 0.30 g (0.73 mmol) of **23** in 15 mL of HOAc was refluxed for 1 h with a few drops of concentrated H_2SO_4 to yield 0.25 g (87%) of **24:** mp 230.–230.5 °C; IR 1667 cm^{-1}; mass spectrum *m/e* 392 (M^+) and 364.

Retro-pinacol Rearrangement of 4,5-Dihydro-4-oxo-5-(4,5-phenanthrylene)pyrene (24). A solution of 0.45 g (1.1 mmol) of **24** in 45 mL of HOAc was refluxed for 18 h with HI (57%, 1 mL) and red P_4 (1.0 g) to give 0.39 g (91%) of tetrabenzo[*de,hi,mn,qr*]naphthacene (**25**): mp 296–297 °C; mass spectrum *m/e* 376 (M^+) and 202; NMR (C_5D_5N) δ 8.00–8.52 (16 H, m).

4,5-Dihydro-4-hydroxy-5-(4,5-phenanthrylene)pyrene (26). A solution of **24** (0.5 g, 1.3 mmol) in THF (60 mL) was refluxed with $LiAlH_4$ (0.12 g, 3.2 mmol) for 3 h to afford 0.42 g (84%) of **26:** mp 151–152 °C (dec); IR 3570 and 3460 cm^{-1}; NMR (C_6D_6) δ 1.50 (1 H, d, J = 6.3 Hz), 5.08 (1 H, d), and 6.75–7.85 (16 H, m).

Alcohol **26** (0.37 g, 74%) was also isolated by the reaction of **24** (0.5 g, 1.3 mmol) with hydrazine hydrate (90%, 0.2 g, 4 mmol) and KOH (0.1 g, 1.8 mmol) in diethylene glycol (60 mL) at 100–110 °C for 1 h and then at 200–210 °C for additional 3 h.

Wagner–Meerwein Rearrangement of 26. A mixture of **26** (0.25 g, 0.63 mmol), HI (57%, 0.14 mL), and red P_4 (0.07 g) in HOAc (20 mL) was refluxed for 30 min; 0.21 g (88%) of **25** was obtained.

Registry No.—**1**, 203-64-5; **2**, 129-00-0; **3**, 64884-30-6; **4**, 64884-31-7; **5**, 3353-12-6; **6**, 15679-25-1; **7**, 5660-87-7; **8**, 64884-32-8; **9**, 64884-33-9; **10**, 64900-53-4; **11**, 64884-34-0; **12**, 64884-35-1; **13**, 64884-36-2; **14**, 64884-37-3; **15**, **64884-38-4**; **16**, 64884-39-5; **17**, 64884-40-8; **18**, 23702-49-0; **19**, 194-03-6; **20**, 5737-13-3; **21**, 64884-41-9; **22**, 64884-42-0; **23**, 64884-43-1; **24**, 64913-41-3; **25**, 385-13-7; **26**, 64884-44-2; BuBr, 109-65-9; EtOAc, 141-78-6.

References and Notes

(1) O. Kruber, *Ber. Dtsch. Chem. Ges.*, **67**, 1000 (1934).
(2) For examples, see: G. Wittig and G. Pieper, *Ann.*, **558**, 207, 218 (1947); J. Douris and L. Giral, *Bull. Soc. Chim. Fr.*, **1970**, 3530.
(3) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).
(4) R. Criegee, E. Höger, G. Huber, P. Kruck, F. Marktscheffel, and H. Schellenberger, *Justus Liebigs Ann. Chem.*, **599**, 81 (1956).
(5) H. Medenwald, *Chem. Ber.*, **86**, 287 (1953).
(6) V. G. Simikov, V. A. Yakobi, V. L. Plakidin, and P. P. Karpukhin, *Zh. Prikl. Khim.*, **46**, 2353 (1973).
(7) F. M. Dean, J. Goodchild, and A. W. Hill, *J. Chem. Soc. C*, 2192 (1969).
(8) T. Ooya, M. Minabe, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, to be published.
(9) M. Minabe, M. Yoshida, M. Fujimoto, and K. Suzuki, *J. Org. Chem.*, **41**, 1935 (1976).
(10) N. Campbell and D. H. Reid, *J. Chem. Soc.*, 3281 (1952).
(11) T. Kimura, M. Minabe, M. Tsubota, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **50**, 258 (1977).
(12) G. Sugowdz, P. J. Collin, and W. H. F. Sasse, *Tetrahedron Lett.*, 3843 (1969).

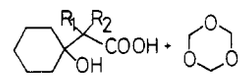
A New Preparative Method for α,β-Unsaturated δ-Lactones from the Reaction of 3-Hydroxy Acids with 1,3,5-Trioxane

Tsutomu Fujita, Shoji Watanabe,* Kyoichi Suga, Ryuichi Yanagi, and Fusao Tsukagoshi

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba, Japan 280

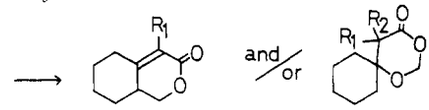
Received August 2, 1977

Various methods for the preparation of lactones are well known; for example, saturated lactones are prepared by oxidation of cyclobutanones,[1] reduction of cyclic carboxylic acid anhydrides,[2] cyclization of 4-hydroxy acids,[3] and so on. Synthetic methods for unsaturated lactones[4] and α-methylene lactones[5] are also well known. However, a synthesis of α,β-unsaturated δ-lactones from 3-hydroxy acids has not been known. We now wish to report a synthesis of α,β-unsaturated δ-lactones **2** from the reaction of 3-hydroxy acids **1** with



1

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = C_2H_5$; $R_2 = H$
d, $R_1 = n\text{-}C_3H_7$; $R_2 = H$
e, $R_1 = i\text{-}C_3H_7$; $R_2 = H$
f, $R_1 = n\text{-}C_4H_9$; $R_2 = H$
g, $R_1 = R_2 = CH_3$



2

a, $R_1 = H$
b, $R_1 = CH_3$
c, $R_1 = C_2H_5$
d, $R_1 = n\text{-}C_3H_7$
e, $R_1 = i\text{-}C_3H_7$
f, $R_1 = n\text{-}C_4H_9$

3

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = C_2H_5$; $R_2 = H$
d, $R_1 = n\text{-}C_3H_7$; $R_2 = H$
e, $R_1 = i\text{-}C_3H_7$; $R_2 = H$
f, $R_1 = n\text{-}C_4H_9$; $R_2 = H$
g, $R_1 = R_2 = CH_3$

1,3,5-trioxane or paraformaldehyde. When a mixture of 2-(1′-hydroxycyclohexan-1′-yl)propionic acid (**1b**), 1,3,5-trioxane, and sulfuric acid was refluxed in acetic acid for 0.5

Table I. Reaction of 2-(1′-Hydroxycyclohexan-1′-yl)propionic Acid (1b) with 1,3,5-Trioxane or Paraformaldehyde in the Presence of Acidic Materials[a]

Acidic materials	Yield (%)[b] of **3b**[f]	Yield (%)[b] of **2b**[g]	Yield (%)[b] of **3b**[g]
H_2SO_4	71	88[d]	
	(55)[c]	(80)	*c,e*
H_3PO_4	33	61	
	(33)[c]	(1)	(55)[c]
$ZnCl_2$	19	61	23
	(19)[c]	(5)	(48)[c]
$AlCl_3$	96	97	
	(78)[c]	(52)	(25)[c]
BF_3–ether complex	99	66	
	(59)[c]	(56)	*e*
Polyphosphoric acid	99	50	
	(48)[c]	(51)	*c*

[a] 3-Hydroxy acid **1b** (8.6 g, 50 mmol), 1,3,5-trioxane (2.7 g, 30 mmol), acidic materials (25 mmol), and acetic acid (50 mL) were used. [b] The yield are based on 3-hydroxy acid used. [c] In these cases, paraformaldehyde was used. [d] Reaction time was 0.5 h. [e] Reaction time was 2 h. [f] At 25 °C for 8 h. [g] At 118 °C for 8 h.

0022-3263/78/1943-1248$01.00/0