Electrophilic Substitution of 4*H*-Cyclopenta[*def*]phenanthrene Derivatives

Masaaki Yoshida,* Hiroshi Hirota,[†] Masahiro Minabe, and Kazuo Suzuki

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

The nitration and the Friedel–Crafts acetylation of nitro-, acetyl-, and bromo-4*H*-cyclopenta[*def*]phenanthrene were carried out. The reactions of 1, 2, and 3 isomers gave predominantly 5 and 7 derivatives, accompanied by 8- or 9-substituted compounds, depending upon the substituent effect. The reactions of 8 isomers afforded the compounds attacked at the 2 and 6 positions, different from those of the other analogues. The structures of over 50 disubstituted compounds were assigned by ^{1}H NMR spectra.

In the electrophilic substitution of 4*H*-cyclopenta[*def*]phenanthrene (**1**) (*1*), we have reported on nitration (*2*), bromination (*3*), and acetylation (*4*) to react differently from the reactivities of phenanthrene, fluorene, and acenaphthene which can be regarded as partial structures in molecule **1**. The following proportions were obtained: 1 (40%), 2 (5%), 3 (30%), and 8 derivatives (25%) on the nitration of **1** with nitric acid (d = 1.42 g cm^{-3}), 1 (80%), 3 (5%) and 8 bromides (15%) on the bromination in chloroform, and 1 (46%), 2 (14%), 3 (39%), and 8 ketones (1%) on the acetylation in nitrobenzene.

The present paper deals with the nitration and the Friedel–Crafts acetylation of nitro, acetyl, and bromo derivatives of **1** and shows the ^{1}H NMR spectral assignment of the disubstituted products, in order to investigate the substituent effect on these electrophilic reactions.

Results and Discussion

The nitration of nitro compounds **2–5**, ketones **6–9**, and bromides **10–13** is summarized in Table I. The Friedel-Crafts aceylation of **2-9** is listed in Table II (Figure 1).

The component of these disubstituted isomers was independent of the reaction temperature as is shown in typical runs of **10** (Table I). Therefore, the formation of these compounds may be caused by kinetic control.

The positions of the entering groups in **2–13** were established by their IR, UV (Table III), and NMR spectra (Table IV). In addition, compounds **36** and **44** were confirmed by nitration of ketones **6** and **8** and by acetylation of nitro isomers **2** and **4**, respectively; and compounds **14, 18, 21, 23–25, 27, 34, 37, 40, 42, 43, 46,** and **47** were estimated in a similar manner and by NMR spectral interpretation. Dinitro derivatives **16, 17, 21,** and **22** were derived from the amides **68, 69, 70,** and **71**, which were obtained by the Schmidt reaction of ketones **36, 48, 43,** and **44**, respectively.

In the NMR spectra, the protons located at the ortho or peri positions of the substituents shift to lower fields than those of the parent **1** because of the deshielding effect. For example, protons H-2 and H-9, adjacent to the 1-nitro group, shift on average ca. 66 and 68 Hz, respectively; H-7 and H-9, adjacent to the 8-nitro group, shift 66 and 88 Hz, respectively. H-9 for **17** shifts 123 Hz, and H-2 and H-8 for **18** shift 43 and 60 Hz, respectively. These values for protons interposed by two functional groups appear to be roughly an additive property of each group (e.g., for **17, 21, 22, 30, 31, 33, 43, 44, 48, 51, 53, 56, 60,** and **62**), but, when the two substituents are adjacent to each other (e.g., **18, 38, 39, 52, 57,** and **64**), their ortho and peri protons cause minor shifts, because the coplanarity of the two groups is hindered sterically and the deshielding effect decreases.

Table I. Nitration of Monosubstituted 4*H*-Cyclopenta[*def*]phenanthrenes

reactant	yield, %	proportion of isomers, % 1	2	3	5	6	7	8	9	recovd, %
2	85				23		64		13	4
6	87			4	25		46	9	16	
10	24			10	21		28	14		59
10[a]	56			10	22		28	14		40
3	84				35		53		12	5
7	80			3	28		38		23	8
11	56	12			21		46			15
4	87				25		56		19	5
8	42				30		41		29	42
12	29	3					48			64
5	88	14			20	18	41			3
9	90	7	18		6	21	45			
13	12	33		30					32	74

[a] The reaction was carried out at 60–65 °C for 3 min.

Table II. Acetylation of Monosubstituted 4*H*-Cyclopenta[*def*]phenanthrenes

reactant	yield, %	proportion of isomers, % 1	2	5	6	7	recovd, %
2	35			31	7	62	54
6	40			28	6	66	51
3	35			36	5	59	60
7	17			42	8	50	82
4	25			32	11	57	69
8	15			24	8	68	73
5	17	33		22	18	0	79
9	11		16	21	63		82

Also the torsional effect of the functional groups is observed at ν(C=O) and $\nu(NO_2)$ in the IR spectra. These peaks shift to higher frequency than those of the other analogues. The magnitude of the movements of the two signals appears to have a complementarity.

The UV spectra of the products substituted at the 2 or 6 position show the strong π–π* transition at ca. 300 nm (e.g., **49** and **51** in Figure 2) apart from the other disubstituted compounds. The absorption maxima of **52** is transformed comparably because of the torsional effect of the system; indeed, the crystal of **52** is colorless while the other nitro homologues are yellow.

Experimental Section

All of the melting points are uncorrected. The instruments used in this experiment were the same as those described elsewhere (*2*). The UV and NMR spectra were measured in $CHCl_3$ and $CDCl_3$, respectively. The high-performance liquid-phase chromatograph was obtained on a FLC-150 instrument (Jasco) attached to a UV detector (λ 254 nm) using a reversed phase partition type SS-10-ODS column (Jasco, 25 cm) with isooctane/EtOAc (80/20 by volume) as a mobile phase and a

---

[†] Present address: Shiratori Pharmaceutical Co. Ltd., Narashino 275, Japan.

0021-9568/81/1726-0220$01.25/0

Table III. Physical Properties of Disubstituted 4*H*-Cyclopenta[*def*]phenanthrenes

compd	mp, °C	IR data (KBr), cm^{-1}	UV λ_{max}, nm (log ϵ), in $CHCl_3$	HPLC rt, min
14	254–255 decomp	1525, 1514, 1343, 1330	364 (4.05), 260 (4.34)	4.1
15	265–266 decomp	1527, 1515, 1503, 1338, 1309	306 (4.52), 269 (4.50)	5.5
16	243–244 decomp	1512, 1330	360 (4.02), 260 (4.37)	11.3
17	239–240 decomp	1538, 1518, 1336, 1327	370 (3.83), 305 (3.80)	9.0
18	230–231 decomp	1530, 1518, 1364, 1340	349 (4.24), 258 (4.37)	9.8
19	243–244 decomp	1524, 1334	382 (3.49), 306 (4.30), 268 (4.35), 257 (4.34)	4.6
20	274–275 decomp	1529, 1337	342 (3.95), 272 (4.40)	
21	263–264 decomp	1524, 1341, 1328	370 (3.40), 330 (3.77), 283 (4.58), 271 (4.45)	6.8
22	237–238 decomp	1520, 1340	346 (4.09), 313 (4.13)	6.5
23	267–268 decomp	1529, 1518, 1335, 1325	350 (3.90), 320 (4.15), 258 (4.30)	4.6
24[a]	193–193.5	1668	322 (4.08), 258 (4.58), 244 (4.51)	10.7
25[a]	174–175	1671	330 (3.78), 286 (4.78), 275 (4.62), 267 (4.63)	12.3
26[a]	197–197.5	1662	330 (4.60), 301 (3.98), 257 (4.48)	13.8
27	171–171.5	1666	373 (3.43), 355 (3.31), 286 (4.51), 278 (4.43), 267 (4.40), 242 (4.33)	7.5
28[a]	258–259	1673	317 (4.23), 298 (4.25), 277 (4.79)	10.0
29	164–165	1660		8.9
30	188–189	1661	370 (3.40), 330 (3.77), 283 (4.58), 271 (4.45)	9.8
31	232–233	1669	376 (2.95), 338 (4.13), 328 (4.17), 299 (4.10), 285 (4.00), 256 (4.62)	12.2
32	214–215	1675	376 (3.06), 324 (4.00), 297 (4.19), 285 (4.18), 256 (4.55)	13.1
33	238–239 decomp	1675, 1527, 1339	363 (4.20), 280 (4.10), 266 (4.22)	4.2
34	222–223 decomp	1666, 1525, 1333	345 (4.09), 258 (4.45)	6.1
35	234–234.5 decomp	1668, 1525, 1329	306 (4.62), 279 (4.53)	8.4
36	206–207 decomp	1664, 1520, 1504, 1331, 1313	348 (4.01), 313 (3.95), 256 (4.57)	12.2
37	265–266 decomp	1663, 1526, 1322	360 (3.78), 298 (4.08), 288 (4.05)	11.0
38	215–216 decomp	1678, 1525, 1359, 1346	320 (3.82), 252 (4.47)	8.4
39	187–188 decomp	1697, 1526, 1332	332 (4.23), 284 (4.66)	5.2
40	206–207 decomp	1673, 1533, 1334	344 (4.03), 288 (4.33), 256 (4.54)	7.4
41	268–269 decomp	1673, 1527, 1334	332 (4.23), 284 (4.66)	8.1
42	205–206 decomp	1677, 1513, 1505, 1323, 1310	350 (3.99), 291 (4.37), 278 (4.33), 263 (4.55), 257 (4.47)	8.8
43	213–214 decomp	1677, 1522, 1325	360 (3.85), 288 (4.30), 260 (4.47)	6.4
44	275–276 decomp	1669, 1529, 1332	346 (3.91), 300 (3.96), 287 (3.98), 255 (4.47)	7.0
45	262–263 decomp	1669, 1524, 1333	320 (4.21), 300 (4.41), 280 (4.53)	7.6
46	240–241 decomp	1672, 1507, 1325, 1308	348 (3.99), 307 (3.82), 255 (4.50)	7.6
47	230–231 decomp	1674, 1513, 1332	358 (3.93), 308 (4.11), 252 (4.44)	6.5
48	214–215 decomp	1667, 1516, 1330	360 (3.85), 300 (3.81)	5.2
49	218–219 decomp	1663, 1523, 1338	303 (4.41)	4.6
50	230–231 decomp	1664, 1526, 1340	340 (3.94), 290 (4.15), 255 (4.44)	6.4
51	245–246 decomp	1665, 1529, 1338	296 (4.47)	7.1
52	183–184 decomp	1678, 1525, 1359, 1346	252 (4.63)	7.0
53	224–225 decomp	1537, 1366	354 (3.86), 301 (3.72)	3.9
54	238–239 decomp	1525, 1336	353 (4.01), 301 (3.70), 290 (3.70), 248 (4.53)	3.7
55	236–237 decomp	1515, 1335	350 (3.89), 290 (3.88)	6.5
56	243–244 decomp	1524, 1336	364 (3.71), 296 (3.76), 240 (4.56)	5.4
57	161–162 decomp	1524, 1332		4.4
58	202–203 decomp	1524, 1335	350 (3.55), 302 (3.64), 248 (4.62)	4.0
59	234–235 decomp	1528, 1337	340 (3.89), 285 (4.36), 273 (4.37), 242 (4.45)	4.6
60	208–209 decomp	1516, 1328	360 (3.61), 300 (3.64), 290 (3.79)	4.0
61	211–212 decomp	1512, 1330	356 (3.90), 302 (3.54), 245 (4.61)	3.9
62	231–232 decomp	1511, 1331	354 (3.95), 292 (3.92), 280 (3.98)	6.2
63	204–205 decomp	1531, 1332	352 (3.98), 299 (3.71), 250 (4.49)	3.7
64	214–215 decomp	1524, 1366	354 (3.32), 338 (3.30), 318 (3.70), 296 (3.81), 252 (4.58)	4.7
65[b]	287–288 decomp	1522, 1332		
66	237–238 decomp	1670, 1520, 1332	350 (4.40), 288 (3.67)	
67	204–205 decomp	1526, 1334		
68	270–271 decomp	3350, 1656, 1552, 1307		
69	266–267 decomp	3250, 1661, 1527, 1321		
70	283–284 decomp	3270, 1664, 1570, 1317		
71	273–274 decomp	3260, 1653, 1544, 1330		
72	377–378 decomp	3640, 1652		

[a] Reference 4. [b] Reference 2.

flow rate of 1.0 mL/min; **1** was used as an internal standard (retention time 3.4 min). All of the elemental analyses (error ±0.3% for C, H, N) and the mass spectra of these new compounds gave satisfactory results.

Nitration of Monosubstituted 4H-Cyclopenta[def]phenanthrenes. General Procedure. The finely powdered mononitro substrate (235 mg, 1 mmol) was added to HNO_3 (d = 1.42 g cm^{-3}, 10 mL). The reaction mixture was stirred at 70–80 °C for 5 min and then poured into water. The precipitate was extracted with benzene, and the extract was washed with aqueous Na_2CO_3 (5%). A part of the organic layer was submitted to HPLC after mixing with **1** to determine the components. The residual portion was chromatographed in benzene on a silica gel column, and then each eluate was evaporated and the residues were recrystallized from benzene to afford pure compounds. The reaction of monoacetyl derivatives was carried out at 40–43 °C for 3 min. Nitration of monobromo substrates was done at 35–40 °C for 3 min. Carbon tetrachloride was used as the eluent for separation by column chromatography.

Acetylation of Monosubstituted 1. General Procedure. A solution of substrate (1 mmol) in $PhNO_2$ (10 mL) was added to a mixture of $AlCl_3$ (0.54 g, 3.4 mmol), Ac_2O (0.12 mL, 1.3 mmol) in $PhNO_2$ (10 mL). After stirring at 20 °C for 20 h, the

Table IV. NMR Assignment of Disubstituted 4*H*-Cyclopenta[*def*]phenanthrenes

	chemical shift δ, *J* value, Hz (in CDCl$_3$)[g]									
compd	Me[a]	H-4	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-9
14		4.92 s	NO$_2$	8.73 d, 7.8	7.90 d, 7.8	NO$_2$	8.52 d, 8.4	8.03 d, 8.4	8.16 d, 9.0	8.97 d, 9.0
15		4.53 s	NO$_2$	8.73 d, 7.8	7.88 d, 7.8	8.61 s	NO$_2$	8.90 s	8.21 d, 9.0	8.90 d, 9.0
16[b]		4.61 s	NO$_2$	8.67 d, 7.8	8.00 d, 7.8	8.00 d, 7.8	8.67 d, 7.8	NO$_2$	8.76 s	8.76 s
17		4.45 s	NO$_2$	8.71 d, 7.8	7.83		7.95 m	8.46–8.68 m	NO$_2$	9.76 s
18		4.49 s	NO$_2$	8.32 d, 7.8	7.78			7.96 m	8.73 s	NO$_2$
19		4.96 s	8.94 s	NO$_2$	8.70 s	NO$_2$	8.67 d, 8.4	7.97		8.13 m
20[b]		4.13 s	8.23 s	NO$_2$	8.08 s	8.08 s	NO$_2$	8.23 s	8.15 s	8.15 s
21[b]		4.38 s	9.11 s	NO$_2$	8.45 s	7.69		8.11 m	9.02 s	NO$_2$
22		5.35 s	8.06 d, 8.4	8.53 d, 8.4	NO$_2$	NO$_2$	8.53 d, 8.4	8.06 d, 8.4	8.12 s	8.12 s
23		4.92 s	8.86 d, 8.4	8.58 d, 8.4	NO$_2$	7.96		8.07 m	9.17 s	NO$_2$
24[c]	2.75, 2.79	4.51 s	Ac	8.13 d, 7.8	7.64 d, 7.8	Ac	8.07 d, 8.4	7.77 d, 8.4	7.85 d, 9.0	8.90 d, 9.0
25[c]	2.78, 2.80	4.30 s	Ac	8.18 d, 7.8	7.69 d, 7.8	8.23 s	Ac	8.40 s	7.93 d, 9.0	8.85 d, 9.0
26[c]	2.80, 2.80	4.25 s	Ac	8.13 d, 7.8	7.62 d, 7.8	7.62 d, 7.8	8.13 d, 7.8	Ac	8.90 s	8.90 s
27	2.96, 2.96	4.70 s	8.52 s	Ac	8.38 s	Ac	8.23 d, 8.4	7.85		7.98 m
28[c]	7.29, 7.29	4.35 s	8.43 s	Ac	8.26 s	8.26 s	Ac	8.43 s	7.88 s	7.88 s
29	2.83, 2.89	4.38 s	8.57 s	Ac	8.37 s	7.74	7.83 m	8.68–8.92 m	Ac	8.54 s
30	2.79, 2.86	4.34 s	9.47 s	Ac	8.37 s	7.69		7.90 m	8.53 s	Ac
31	2.86, 2.86	4.96 s	7.94 d, 8.4	8.25 d, 8.4	Ac	Ac	8.25 d, 8.4	7.94 d, 8.4	7.98 s	7.98 s
32	2.82, 2.90	4.66 s	8.93 d, 8.4	8.20 d, 8.4	Ac	7.70		8.06 m	8.63 s	Ac
33	2.89	4.86 s	Ac	8.94 s	NO$_2$	7.77		7.90 m	8.17 d, 9.0	8.94 d, 9.0
34	2.86	4.77 s	Ac	8.30 d, 7.8	7.82 d, 7.8	NO$_2$	8.43 d, 8.4	7.93 d, 8.4	7.98 d, 9.0	9.08 d, 9.0
35	2.83	4.47 s	Ac	8.35 d, 7.8	7.84 d, 7.8	8.56 s	NO$_2$	8.85 s	8.08 d, 9.0	9.05 d, 9.0
36	2.85	4.44 s	Ac	8.31 d, 7.8	7.75 d, 7.8	7.80 d, 7.8	8.63 d, 7.8	NO$_2$	8.80 d, 9.0	9.11 d, 9.0
37[b]	2.78	4.40 s	Ac	8.40 d, 7.8	7.92 d, 7.8	7.71	7.90 m	8.28–8.48 m	NO$_2$	9.62 s
38	2.80	4.43 s	Ac	7.99 d, 7.8	7.73			7.94 m	8.55 s	NO$_2$
39	2.67	4.68 s	8.03 s	Ac	NO$_2$	7.67				7.86 m
40	2.83	4.82 s	8.53 s	Ac	8.39 s	NO$_2$	8.42 d, 8.4	7.94 d, 8.4	7.90 d, 9.0	8.08 d, 9.0
41	2.82	4.48 s	8.54 s	Ac	8.37 s	8.54 s	NO$_2$	8.82 s	8.00 s	8.00 s
42	2.84	4.47 s	NO$_2$	8.70 d, 7.8	7.82 d, 7.8	8.41 s	Ac	8.56 s	8.18 d, 9.0	8.82 d, 9.0
43	2.86	4.43 s	9.27 s	Ac	8.42 s	7.78		8.00 m	8.99 s	NO$_2$
44	2.81	5.13 s	7.92 d, 8.4	8.21 d, 8.4	Ac	NO$_2$	8.42 d, 8.4	7.92 d, 8.4	8.00 s	8.00 s
45[d]	2.81	4.80 s	8.95 s	NO$_2$	8.63 s	Ac	8.31 d, 8.4	8.04		8.25 m
46	2.85	4.77 s	NO$_2$	8.72 d, 7.8	7.88 d, 7.8	Ac	8.29 d, 8.4	8.02 d, 8.4	8.16 d, 9.0	8.92 d, 9.0
47	2.84	4.71 s	8.76 d, 8.4	8.29 d, 8.4	Ac	7.89		8.01 m	9.07 s	NO$_2$
48	2.93	4.42 s	NO$_2$	8.65 d, 7.8	7.72		7.90 m	8.58–8.78 m	Ac	9.39 s
49	2.90	4.47 s	8.95 s	NO$_2$	8.64 s	7.81	7.91 m	8.76–8.92 m	Ac	8.55 s
50	2.90	4.79 s	8.94 d, 8.4	8.39 d, 8.4	NO$_2$	7.85		7.94 m	8.65 s	Ac
51	2.89	4.44 s	9.78 s	NO$_2$	8.52 s	7.86		7.93 m	8.60 s	Ac
52	2.85	4.45 s	NO$_2$	8.24 d, 7.8	7.72			7.92 m	8.33 s	Ac
53		4.72 s	Br	8.59 s	NO$_2$	7.72		7.91 m	7.97 d, 9.0	8.09 d, 9.0
54		4.75 s	Br	7.91 d, 7.8	7.61 d, 7.8	NO$_2$	8.41 d, 8.4	7.91 d, 8.4	7.94 d, 9.0	8.10 d, 9.0
55		4.35 s	Br	7.89 d, 7.8	7.58 d, 7.8	7.74 d, 7.8	8.62 d, 7.8	NO$_2$	8.78 d, 9.0	8.13 d, 9.0
56		4.32 s	Br	7.69			7.94 m	8.46–8.68 m	NO$_2$	8.97 s
57		4.31 s	NO$_2$	Br	7.57				7.94 m	7.92 d, 9.0
58		4.72 s	8.09 s	Br	7.87–8.01 m	NO$_2$	8.44 d, 8.4	7.87		8.01 m
59		4.39 s	NO$_2$	8.60 d, 7.8	7.97 d, 7.8	7.87 s	Br	8.05 s	7.97 d, 9.0	8.76 d, 9.0
60		4.42 s	NO$_2$	8.61 s	Br	7.72		7.88 m	8.04 d, 9.0	8.59 d, 9.0
61		4.32 s	NO$_2$	8.61 d, 7.8	7.67–7.83 m	Br	7.67	7.83 m	8.03 d, 9.0	8.68 d, 9.0
62		4.40 s	NO$_2$	8.58 d, 7.8	7.66		7.87 m	7.92–8.15 m	Br	9.02 s
63		4.83 s	7.65–7.93 m	8.28 d, 8.4	NO$_2$	7.65		7.93 m	Br	8.06 s
64		4.33 s	8.01–8.16 m	7.62				7.94 m	Br	NO$_2$
65[e]		3.99 s	8.18 s	NO$_2$	8.35 s	8.35 s	NO$_2$	8.18 s	3.10 s	3.10 s
66	2.76	4.07 s	7.83 s	Ac	8.03 s	8.38 s	NO$_2$	8.11 s	3.27 s	3.27 s
67		3.98 s	7.36 s	Br	7.54 s	8.25 s	NO$_2$	8.07 s	3.21 s	3.21 s
68[b]	2.17	4.36 s	10.21[f] s	7.83 d, 7.8	7.72 d, 7.8	8.03 d, 7.8	8.53 d, 7.8	NO$_2$	8.46 d, 9.0	8.28 d, 9.0
69[b]	2.25	4.12 s	10.34[f] s	7.86 d, 7.8	7.46		7.57 m	7.90–8.21 m	NO$_2$	9.59 s
70[b]	2.16	4.45 s	9.08 s	10.41[f] s	8.32 s	7.76		8.03 m	8.71 s	NO$_2$
71[b]	2.16	4.69 s	7.92	8.12 m	10.21[f] s	NO$_2$	8.29 d, 8.4	7.92		8.12 m
72[b]	2.13	4.32 s	7.88 s	10.10[f] s	7.78 s	7.78 s	10.10[f] s	7.88 s	8.14 s	8.14 s

[a] Singlet. [b] Solvent: Me$_2$SO-d_6. [c] Reference 4. [d] Me$_2$SO-d_6 was used as a solvent at 100 °C. [e] Solvent: pyridine-d_5; ref 2. [f] The proton was assigned to NH. [g] For example, in compd 17, protons H-3, H-5, and H-6 appear at 7.83–7.95 ppm as an unresolved multiplet.

reaction mixture was hydrolyzed and extracted with benzene. The extract was then steam distilled, and the residue was chromatographed in benzene on silica gel column. Each eluate was treated by HPLC and recrystallization.

Nitration of 2-Nitro-8,9-dihydro-4H-cyclopenta[def]-phenanthrene (73). To a solution of 73 (474 mg, 2 mmol) in HOAc (20 mL), a mixed acid (prepared from HNO$_3$, d = 1.42 g cm^{-3}, 0.32 mL, and concentrated H$_2$SO$_4$, 0.55 mL) was added at 80 °C for 5 min. The reaction mixture was stirred at that temperature for an additional 15 min and then poured into water. After extraction, the extract was chromatographed in CCl$_4$ on a silica gel column. The first eluate afforded 3 (115 mg, 24%). The second eluate was evaporated to dryness, and the residue was recrystallized from benzene to give 230 mg (41%) of 2,6-dinitro-8,9-dihydro-4*H*-cyclopenta[*def*]-phenanthrene (65) (*2*).

Nitration of 2-Acetyl-8,9-dihydro-4H-cyclopenta[def]-phenanthrene (74). The powdered 74 (234 mg, 1 mmol) was added to nitric acid (d = 1.42 g cm^{-3}, 10 mL), and the solution was stirred at 30–35 °C for 5 min. The reaction mixture was treated in a similar manner, giving 15 mg (5%) of 65. In addition, 135 mg (48%) of 2-acetyl-6-nitro-8,9-dihydro-4*H*-cyclo-

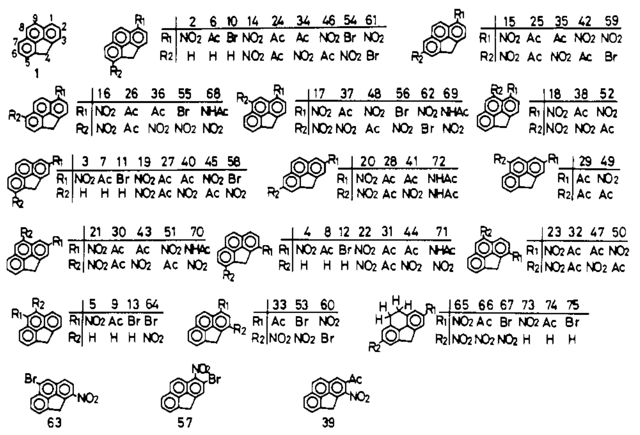

Figure 1.

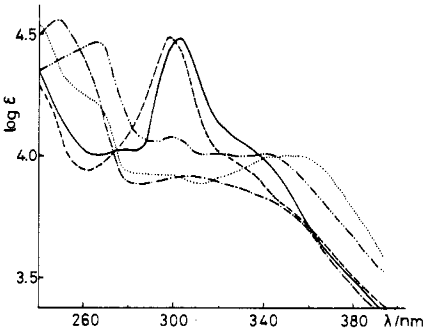

Figure 2. UV spectra of **48** (···), **49** (—), **50** (–··–), **51** (– – –), and **52** (–·–) in $CHCl_3$.

penta[*def*]phenanthrene (**66**) was isolated; **66** was also obtained in a 72% yield by treatment of **73** (237 mg, 1 mmol) with Ac_2O (0.12 mL, 1.3 mmol) and $AlCl_3$ (0.54 g, 4 mmol) in $PhNO_2$ (20 mL) at 20 °C for 20 h.

***Nitration of 2-Bromo-8,9-dihydro-4H-cyclopenta*[*def*]*phenanthrene* (*75*).** A mixed acid (HNO_3, d = 1.42 g cm^{-3},0.32 mL, and concentrated H_2SO_4, 0.55 mL) was added to a solution of **75** (542 mg, 2 mmol) in HOAc (20 mL) at 75–78 °C for 5 min. After stirring for an additional 15 min, the reaction mixture afforded 2-bromo-6-nitro-8,9-dihydro-4*H*-cyclopenta-[*def*]phenanthrene (**67**) (474 mg, 75%).

***Oxidation of 2-Acetyl-6-nitro-8,9-dihydro-4H-cyclopenta*[*def*]*phenanthrene* (*66*).** To a refluxing solution of **66** (130 mg, 0.47 mmol) in HOAc (30 mL), nitric acid (d = 1.42 g cm^{-3}, 5 mL) was added over a period of 10 min, and the refluxing was maintained for an additional 1 h, yielding 21 mg (16%) of **41**.

***Schmidt Reaction of 36*.** A mixture of **36** (180 mg, 0.65 mmol), NaN_3 (90 mg, 1.38 mmol), and Cl_3CCO_2H (3.5 g) was stirred at 90–95 °C for 6 h. To the reaction mixture, 30 mL of water was added, and the precipitate was chromatographed in benzene on a silica gel column. The eluate yielded 23 mg (13%) of **36**. Also, 88 mg (46%) of *N*-acetyl-7-nitro-4*H*-cyclopenta[*def*]phenanthren-1-amine (**68**) was obtained by extraction of the column with EtOAc.

In a similar manner, the following amines were obtained from the corresponding acetyl compounds: *N*-acetyl-8-nitro-4*H*-cyclopenta[*def*]phenanthren-1-amine (**69**, yield 65%); *N*-acetyl-9-nitro-4*H*-cyclopenta[*def*]phenanthren-2-amine (**70**, yield 66%); *N*-acetyl-5-nitro-4*H*-cyclopenta[*def*]phenanthren-3-amine (**71**, yield 66%); *N*,*N′*-diacetyl-4*H*-cyclopenta[*def*]-phenanthrene-2,6-diamine (**72**, yield 71%).

***Dinitro Compounds from Amides*.** The amide **68** (75 mg, 0.26 mmol) in HOEt (10 mL) was refluxed with concentrated HCl (8 mL) for 3 h and was cooled to room temperature to give the hydrochloride. The salt was stirred in HOEt (5 mL) and benzene (5 mL) with aqueous ammonia (28%, 0.1 mL) at room temperature for 1 min. After extraction with benzene, the extract was evaporated to dryness, and the residue was added dropwise to *m*-chloroperoxybenzoic acid (350 mg, 2 mmol) in $CHCl_3$ (8 mL) at 0 °C for 10 min. Then the temperature of the mixture was elevated to 30 °C for a period of 30 min. The resulting mixture was poured into water and extracted with benzene. The organic layer was evaporated to dryness, and the residue was chromatographed in benzene on silica gel to afford 35 mg (48%) of **16**. By a similar method, **17**, **20**, **21**, and **22** were obtained from **69**, **72**, **70**, and **71** in yields of 24%, 25%, 31%, and 46%, respectively.

Literature Cited

(1) Kruber, O. *Ber. Dtsch. Chem. Ges.* **1934**, *67*, 1000.
(2) Yoshida, M.; Nagayama, S.; Minabe, M.; Suzuki, K. *J. Org. Chem.* **1979**, *44*, 1915.
(3) Yoshida, M.; Minabe, M.; Suzuki, K. *J. Org. Chem.* **1979**, *44*, 3029.
(4) Yoshida, M.; Hishida, K.; Minabe, M.; Suzuki, K. *J. Org. Chem.* **1980**, *45*, 1783.

Received for review July 7, 1980. Accepted November 10, 1980.

Synthesis of Potential Juvenogen Insecticides. 1. Tetrahydrofuran and Tetrahydropyran Ether Derivatives

Jitka Kahovcová* and Miroslav Romaňuk

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

A series of new tetrahydrofuran and tetrahydropyran ethers with acyl components in the molecules was prepared.

As part of a program aimed at the synthesis of new compounds with selective juvenile hormone activity, we have prepared a series of new ethers derived from tetrahydrofuran and tetrahydropyran and their halogen derivatives (Table I).

Some of the synthesized compounds possess an appreciable juvenile hormone activity as well as proper lipophilicity, low volatility, and other physicochemical properties desirable for practical use.

Experimental Section

All of the boiling points are uncorrected. IR, mass, and ^1H NMR spectra were recorded on a UR 20 spectrophotometer (CCl_4, $CHCl_3$), an AEI MS-902 spectrometer at 70-eV ionization potential, and a Varian HA-60 or HA-100 spectrometer ($CDCl_3$, Me_4Si), respectively. The reaction course and the purity of the

0021-9568/81/1726-0223$01.25/0