

Available online at www.sciencedirect.com



Tetrahedron

Tetrahedron 60 (2004) 10883-10886

# Photoinduced ene-reaction of 9-methylene-9,10-dihydrophenanthrene with alkenes

Akira Sugimoto, Ryoichi Hiraoka, Masahiro Kanayama Yasueda, Hirofumi Mukae and Kazuhiko Mizuno<sup>\*</sup>

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

Received 3 August 2004; revised 10 September 2004; accepted 13 September 2004

Available online 1 October 2004

Abstract—Irradiation of 9-methylene-9,10-dihydrophenanthrene (1) in the presence of 1,1-diphenylethene or styrene in benzene afforded ene-reaction adduct in good yield. In the absence of arylalkenes, the dimerized product of 1, 9-[2-(9-phenanthryl)ethyl]-9,10-dihydrophenanthrene, and 9-methylphenanthrene were obtained as major products. © 2004 Elsevier Ltd. All rights reserved.

# 1. Introduction

Previously, we have reported the chemical properties of 9-methylene-9,10-dihydrophenanthrene (1) which was prepared by the photolysis of 9-(2-anilinoethyl)phenanthrene<sup>1,2</sup> (Eq. 1). Similarly, 1-methylene-1,2-dihydronaphthalene and 2-methylene-2,3-dihydrobenzo[b]thiophene were also prepared from the corresponding 2-anilinoethyl derivatives and their chemical properties were reported.<sup>2</sup> In the photolysis of 2-(2-anilinoethyl)naphthalene, however, 2-[2-(2naphthyl)ethyl]-1,2-dihydronaphthalene (2) as an eneadduct of the corresponding *exo*-methylene compound (3) with another 3 (Eq. 2), was exclusively obtained and neither 3 nor 2-methylnaphthalene was obtained.<sup>3</sup> Lots of enereactions have been reported so far and their mechanisms have been discussed in relation to the Diels-Alder reaction.<sup>4–8</sup> However, photoinduced ene-reactions are less known,<sup>9–12</sup> because [2+2]photocycloaddition proceeds predominantly.<sup>13</sup> The chemical properties of 5-methylene-1,3-cyclohexadiene and its benzologues<sup>14–23</sup> have also been attracted considerable attention from the synthetic and mechanistic viewpoints, but photochemistry of them was rarely noted. We now report the photoinduced ene-reaction of 1 to clarify the photochemical reactivity of  $1.^3$ 



2. Results and discussion

A degassed benzene solution of 1 in a sealed Pyrex-tube was irradiated with a 300 W high-pressure mercury lamp. The reaction products obtained were 9-[2-(9-phenanthryl)ethyl]-9,10-dihydrophenanthrene (4) and 9-methylphenanthrene (5) (Eq. 3) and no other product was detected by <sup>1</sup>H NMR

*Keywords*: Photoreaction; Ene reaction; Isomerization; Aromatization. \* Corresponding author. Tel./fax: +81 72 254 9289;

e-mail: mizuno@chem.osakafu-u.ac.jp

<sup>0040–4020/\$ -</sup> see front matter @ 2004 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2004.09.032

Solvent	Yield/%		Recovery/%	
	4	5	1	
C <sub>6</sub> H <sub>6</sub>	34	21	45	
$C_{6}H_{12}$	37	31	32	
CH <sub>3</sub> CN	31	69	0	
CH <sub>3</sub> OH	37	63	Trace	

Table 1. Solvent effect on the photoreaction<sup>a</sup> of 1

<sup>a</sup> The values were estimated from the intensities of <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of the irradiated mixture after 8 h irradiation.

spectrum. The formation of **4** and **5** can be readily interpreted by the ene-reaction and 1,3-hydrogen shift reaction, respectively. The former is a photochemically forbidden reaction and the latter is an allowed one if the reactions proceed by a concerted mechanism.<sup>24</sup> From the mechanistic viewpoint, irradiation was carried out in several solvents as shown in Table 1. In all cases, the products were the same as those in benzene. The photoreaction proceeded almost completely in polar solvents, and **5** was obtained as major product, although the yield of **4** did not depend on the solvent polarity. It was suggested that the formation of **5** might involve a polar intermediate.



Based on these results, the photoinduced ene-reaction of 1 in the presence of arylalkenes as enophiles were investigated. Irradiation of a degassed benzene solution of 1 containing a large excess (20-fold excess) of 1,1-diphenylethene afforded 9-(3,3-diphenylpropyl)phenanthrene 6 in a 69% isolated yield. Similar irradiation of 1 in the presence of styrene, 1-phenylpropene, and 1,3-pentadiene gave the corresponding ene-adducts 7–9. However, the photoreaction of 1 with 1-hexene and butyl vinyl ether did not afford ene-products, but 4 and 5. In the cases of stilbene and cinnamaldehyde, 1 was almost recovered. The results are summarized in Table

Table 2. Photoreaction of 1 with alkenes in benzene<sup>a,b</sup>

2. The ene-adducts 6-8 were identified by comparing their spectroscopic data with those of authentic compounds, which were prepared by the other methods without irradiation. The photoproduct 9 was converted into the hydrogenated derivative, 9-hexylphenanthrene, and identified.

The incident light (Pyrex filtered light: >280 nm) is competitively absorbed by 1 ( $\lambda_{max}$ =278 nm) and the added alkenes, although the amounts of alkenes are large excess.<sup>1</sup> 1,1-Diphenylethene, styrene, and 1-phenylpropene reacted with the excited singlet of 1 regioselectively to give substituted propane derivatives 6, 7, and 8, respectively. These ene-adducts bear phenanthrylmethyl group regioselectively to the sterically less-hindered carbon atom of the alkenes. However, irradiation of 1 in the presence of (*E*)stilbene gave only (*Z*)-stilbene and unchanged 1 was recovered, presumably due to most of the light absorption by (*E*)-stilbene. Phenylacetylene reacted with 1 upon irradiation to give a complex mixture.



The photoreaction of 1 in the presence of a large amount of 1,3-pentadiene (120-fold) also afforded an ene-adduct in 15%. However, the less amount of 1,3-pentadiene (20-fold) did not give the ene-adduct, but **5** was obtained in 96% yield. In this case, the excited singlet state of **1** may rearrange to **5** before being trapped by 1,3-pentadiene.

Mono-olefins such as 1-hexene and butyl vinyl ether gave no ene-adduct. These results suggested that the reactive

Alkene <sup>c</sup>	Yield/%			Recovery/%
	Ene-adduct	4	5	1
Ph <sub>2</sub> C=CH <sub>2</sub>	<b>6</b> (69)	nd	nd	nd
PhCH=CH <sub>2</sub>	7 (62)	nd	(4)	(4)
PhCH=CHMe	8 (21)	nd	(7)	(19)
(E)-PhCH=CHPh	(0)	(0)	(0)	(100)
CH <sub>2</sub> =CHCH=CHMe	9 (0)	(0)	96	nd
CH <sub>2</sub> =CHCH=CHMe <sup>d</sup>	9 (15)	(10)	nd	nd
$CH_2 = CH(CH_2)_3 Me$	(0)	(18)	(16)	(44)
Bu-O-CH=CH <sub>2</sub>	(0)	(20)	(12)	(35)
PhCH=CHCHO	(0)	(0)	(0)	(75)

<sup>a</sup> Isolated yields and recoveries were obtained based on 1 used.

<sup>b</sup> nd: not determined.

<sup>c</sup> 20 equiv of an alkene based on **1** used.

<sup>d</sup> 120 equiv of 1,3-pentadiene based on **1** used.

alkene has to be conjugated with a phenyl group or with a C=C double bond. Carbonyl compounds such as 2-propenal,  $\beta$ -ionone, and cinnamaldehyde gave no ene-adduct in detectable amount under similar reaction conditions and unchanged **1** was recovered on irradiation, suggesting that an abstraction of hydrogen atom by carbonyl group did not take place under the reaction conditions.

Compound **1** reacted with typical electron-acceptors such as tetracyanoethene and dimethyl acetylenedicarboxylate in the dark at room temperature to give ene-adducts, respectively. But it did not react with styrene, maleic anhydride, and fumaronitrile.<sup>2</sup> 1,1-Diphenylethene did not react with **1** even in refluxing benzene. On the basis of these observations, the present photoreaction is regarded as a photoinduced ene-reaction, although it has been stated that photo-initiated ene-reactions do not occur at less polar conditions.<sup>13</sup>

As mentioned before,<sup>3</sup> irradiation of 2-(2-anilinoethyl)naphthalene affords the ene-adduct 2 without formation of the exo-methylene compound 3, while that of 9-(2anilinoethyl)phenanthrene affords the *exo*-methylene compound 1 without formation of the ene-adduct 4. These observation may be explained by the difference in their absorption spectra. Thus, the compounds 3 and 1 show an absorption maximum at 297 and 278 nm (log  $\varepsilon = 4.14$ ), respectively.<sup>25</sup> On the other hand, the absorption maximum of 2-(2-anilinoethyl)naphthalene was observed at 276 nm  $(\log \varepsilon = 3.83)$  and that of 9-(2-anilinoethyl)phenanthrene was at 298 nm (log  $\varepsilon = 4.00$ ).<sup>2</sup> Namely, in the case of naphthalene derivative, most of the incident light should be absorbed by the photo-product 3 which may change into the ene-adduct 2. In the case of 1, the starting amine should absorb the incident light preferentially and therefore after the consumption of starting amine, the photo-induced enereaction of **1** might take place.

### 3. Experimental

Mp's were determined with a Yanaco micromelting point apparatus (MP-500) and are uncorrected. Spectra were obtained with a Hitachi infrared spectrophotometer (type-215), an NMR spectrometer (JNM-GX-270) (270 MHz) using tetramethylsilane as internal standard, a gas chromatograph-mass spectrometer (Shimadzu-LKB 9000) (mass), and a Shimadzu UV spectrophotometer (UV-160A).

#### 3.1. Materials

9-Methylene-9,10-dihydrophenanthrene **1** was prepared by the method described previously.<sup>1,2</sup> As **1** gradually changed into the methyl isomer, photoreactions were performed without separation of the two isomers (the starting material **1** was contaminated with 5–10% of **5**). The yields in Tables 1 and 2 are based on the amount of **1** at the start of the irradiation.

#### 3.2. Photoreactions

**3.2.1. Preparative irradiation.** A general procedure is shown for the irradiation of 1 with 1,1-diphenylethene: a

solution of **1** [58 mg, purity 91% contained **1** (0.27 mmol)] and 1,1-diphenylethene (973 mg, 5.4 mmol) in benzene (20 mL) in a Pyrex tube was degassed by three freezepump-thaw cycles under argon, and the tube was sealed under reduced pressure. The solution was irradiated externally with 300 W high-pressure mercury lamp (Eikosha PIH-300) for 8 h at room temperature. After irradiation, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with hexane-benzene (5:1, v/v) to give 3-(9-phenanthryl)-1,1diphenylpropane 6 as a colorless solid (70 mg, 69%), mp 129.5–130.5 °C (from hexane);  $\delta$  (CDCl<sub>3</sub>) 2.53–2.62 (2H, m, CH<sub>2</sub>), 3.05-3.10 (2H, t, CH<sub>2</sub>), 4.05-4.10 (1H, t, CH), and 7.14-7.92 (17H, m) and 8.63-8.74 (2H, m) (together 19H ArH); m/z 372 (M+, 46%), 205 (22), 192 (100), and 191 (29). Found: C, 93.39; H, 6.19. Calcd for C<sub>29</sub>H<sub>24</sub>: C, 93.51; H, 6.49%.

The spectral data of the other photo ene-adducts, **7**, **8**, and **9** isolated from the irradiation mixtures by chromatography were compared with those of the corresponding authentic compounds are identified after hydrogenation.

3.2.2. Preparation of 9-[2-(9-phenanthryl)ethyl]-9,10**dihydrophenanthrene 4.** A solution of **1** [61 mg, purity 90% contained 1 (0.286 mmol)] in acetonitrile (20 mL) was irradiated. Chromatography of the irradiated mixture on silica gel with benzene-hexane (1:3, v/v) gave 4 from the third eluent (12 mg, 22%), mp 153–154 °C (from chloro-form–ethanol);  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 3060, 3030, 3010, 2920, 1500, 1485, 1455, 1440, 880, 740, and 720;  $\lambda_{max}$  (hexane)/ nm 212, 254, and 298 (log  $\varepsilon$  4.79, 4.79, and 4.14);  $\delta$  (CDCl<sub>3</sub>) 1.86–1.95 (2H, m, CH<sub>2</sub>), 2.94–3.28 (5H, m, two CH<sub>2</sub> and CH), and 7.21-7.82 (15H, m) and 8.59-8.69 (2H, m) (together 17H ArH); δ (CDCl<sub>3</sub>) 31.31, 33.90, 34.08, 38.83, 122.40, 123.13, 123.55, 124.14, 124.26, 125.82, 125.88, 126.04, 126.44, 126.54, 127.05, 127.17, 127.47, 127.61, 127.96, 128.32, 129.01, 129.60, 130.67, 131.13, 131.86, 133.66, 134.12, 135.24, 136.41, 140.82; *m*/*z* 384 (M+, 33%), 193 (22), 192 (100), 191 (19), 179 (26), and 178 (27). Found: C, 93.46; H, 6.02. Calcd for C<sub>30</sub>H<sub>24</sub>: C, 93.71; H, 6.29%.

3.2.3. Preparation of authentic compounds. 1,1-Diphenyl-3-(9-phenanthryl)propane 6 (ene-adduct with 1,1diphenylethene) was obtained by the hydrogenation of 3-(9-phenanthryl)-1,1-diphenylpropene (mp 141–141.5 °C) which was prepared by the reaction of methyl 3-(9phenanthryl)propanoate with phenylmagnesium bromide followed by the dehydration and 5% Pd-C catalyzed hydrogenation, mp 128.5–129.5 °C;  $\lambda_{max}$  (hexane)/nm 210, 253, 277, 286, and 298 (log  $\varepsilon$  4.65, 4.74, 4.12, 4.01, and 4.08);  $\delta$  (CDCl<sub>3</sub>) 2.57 (2H, q, J = 7.7 Hz, CH<sub>2</sub>), 3.07 (2H, t, J=7.7 Hz, CH<sub>2</sub>), 4.07 (1H, t, J=7.7 Hz, CH), 7.17–7.21 (2H, m, ArH), 7.28-7.36 (10H, m, ArH), 7.51-7.65 (5H, m, ArH), 7.79 (1H, dd, J=1.5, 7.3 Hz, ArH), 7.90 (1H, d, J= 8.0 Hz, ArH), 8.64 (1H, d, J=7.9 Hz, ArH), 8.72 (1H, d, J=8.2 Hz, ArH);  $\delta$  (CDCl<sub>3</sub>) 32.00, 36.37, 51.52, 122.50, 123.27, 124.42, 126.02, 126.18, 126.22, 126.34, 126.55, 126.65, 128.00, 128.06, 128.60, 129.70, 130.75, 131.18, 131.90, 136.34, 144.82.

## 3.2.4. 3-Phenyl-1-(9-phenanthryl)propane 7. Ene-adduct

with styrene. This compound was prepared by the hydrogenation of 3-(9-phenanthryl)-1-phenylpropene (mp 105–107.5 °C) which was obtained by 3 steps from 9-phenanthrylethenyl phenyl ketone (mp 136.5–138 °C), mp 84–85 °C (from pentane);  $\lambda_{max}$  (hexane)/nm 211, 253, 277, 286, and 298 (log  $\varepsilon$  4.57, 4.77, 4.13, 4.02, and 4.07);  $\delta$ (CDCl<sub>3</sub>) 2.15 (2H, quintet, J=7.7 Hz, CH<sub>2</sub>), 2.79 (2H, t, J=7.7 Hz, CH<sub>2</sub>), 3.13 (2H, t, J=7.7 Hz, CH<sub>2</sub>), 7.15–7.36 (2H, m, ArH), 7.50-7.68 (5H, m, ArH), 7.51-7.65 (5H, m, ArH), 7.81 (1H, d, J=7.5 Hz, ArH), 8.01 (1H, d, J=7.9 Hz, ArH), 8.63 (1H, d, J=8.2 Hz, ArH), 8.72 (1H, d, J=8.2 Hz, ArH); δ (CDCl<sub>3</sub>) 31.89, 33.10, 36.12, 122.48, 123.25. 124.42, 125.88, 125.96, 126.11, 126.15, 126.52, 126.62, 128.05, 128.40, 128.56, 129.67, 130.73, 131.26, 131.91, 136.40, 142.17; m/z 296 (M+, 44%), 192 (100), and 191 (42). Found: C, 93.15; H, 6.8. Calcd for C<sub>23</sub>H<sub>20</sub>: C, 93.2; H, 6.8%.

3.2.5. 1-(9-Phenanthryl)-2-benzylpropane 8. Ene-adduct with 1-phenylpropene. This compound was prepared by the following route: propiophenone to 1-(9-phenanthryl)-2benzoylpropane (mp 140-140.5 °C) and from this to 8, mp 112–115 °C (from pentane);  $\lambda_{max}$  (hexane)/nm 211, 253, 277, 286, and 298 (log  $\varepsilon$  4.56, 4.75, 4.12, 4.03 and 4.12);  $\delta$  $(CDCl_3)$  0.93 (3H, d, J=7.6 Hz,  $CH_3$ ), 2.27 (1H, m, CH), 2.61 (1H, dd, J=7.7, 13.7 Hz, CH<sub>2</sub>), 2.78 (2H, dd, J=8.8, 13.8 Hz, CH<sub>2</sub>), 3.25 (1H, dd, J=5.2, 13.7 Hz, CH<sub>2</sub>), 7.17-7.34 (5H, m, ArH), 7.50-7.66 (5H, m, ArH), 7.78-7.84 (2H, m, ArH), 8.64 (1H, d, J=8.2 Hz, ArH), 8.71 (1H, d, J= 8.2 Hz, ArH); δ (CDCl<sub>3</sub>) 20.15, 36.11, 41.01, 44.26, 122.49, 123.22, 124.73, 125.95, 125.96, 126.07, 126.42, 126.62, 127.52, 128.07, 128.26, 129.36, 129.75, 130.80, 131.45, 131.75, 135.41, 141.19; m/z 310 (M+, 45%), 192 (100), and 191 (73). Found: C, 92.53; H, 6.94. Calcd for C<sub>24</sub>H<sub>22</sub>: C, 92.86; H, 7.14%.

**3.2.6. 9-Hexylphenanthrene.**<sup>26</sup> The hydrogenated product of 9, which corresponds to the ene-adduct with 1,3pentadiene. This was prepared from 9-phenanthrenecarbaldehyde by the reaction with pentylmagnesium bromide followed by dehydration and hydrogenation, mp 78–79 °C (from pentane);  $\lambda_{max}$  (hexane)/nm 253, 277, 285, and 298 (log  $\varepsilon$  4.76, 4.13, 4.00 and 4.06);  $\delta$  (CDCl<sub>3</sub>) 0.90 (3H, t, J=7.1 Hz, CH<sub>3</sub>), 1.25–1.41 (4H, m, CH<sub>2</sub>CH<sub>2</sub>), 1.43– 1.54 (2H, m, CH<sub>2</sub>), 1.81 (2H, quintet, J=7.7 Hz, CH<sub>2</sub>), 3.11 (2H, t, J=7.8 Hz, CH<sub>2</sub>), and 7.52–7.71 (5H, m, ArH), 7.78– 7.84 (1H, m, ArH), 8.03-8.14 (1H, m, ArH), 8.65 (1H, d, J = 8.4 Hz, ArH), and 8.61–8.76 (1H, m, ArH);  $\delta$  (CDCl<sub>3</sub>) 14.40, 22.94, 29.81, 30.49, 32.03, 33.73, 122.48, 123.25, 124.54, 125.86, 125.96, 126.09, 126.48, 126.59, 128.04, 129.63, 130.73, 131.39, 132.00, 137.05; *m/z* 262 (M+, 60%), 191 (100), and 179 (28). Found: C, 91.51; H, 8.66. Calcd for C<sub>20</sub>H<sub>22</sub>: C, 91.55; H, 8.45%.

#### Acknowledgements

This work is partially supported by Tokyo Ohka Foundation

for the Promotion of Science and Technology and by a Grant-in-Aid for Scientific Research (Nos. 15350026 and 16655018) and by a Grant-in-Aid for Scientific Research on Priority Areas (417) (No. 15033264) from the Ministry of Education, Science, Sports, and Culture of Japan.

#### **References and notes**

- 1. Sugimoto, A.; Yoneda, S. J. Chem. Soc., Chem. Commun. 1982, 376–377.
- Sugimoto, A.; Yamano, J.; Yasueda, M.; Yoneda, S. J. Chem. Soc., Perkin Trans. 1 1988, 2579–2584.
- Sugimoto, A.; Sakamoto, S.; Suyama, K.; Yoneda, S. Bull. Chem. Soc. Jpn 1986, 59, 1626–1628.
- Fujita, Y.; Suzuki, S.; Kanahira, K. J. Synth. Org. Chem. Jpn 1983, 41, 1152–1167.
- Oppolzer, W.; Snieckus, V. Angew. Chem., Int. Ed. Engl. 1978, 17, 476–486.
- 6. Oppolzer, W. Angew. Chem., Int. Ed. Engl. 1984, 23, 876-889.
- 7. Carruthers, W. Cycloaddition Reactions in Organic Synthesis; Pergamon: Oxford, 1990; pp 241–268.
- 8. Snider, B. B. Acc. Chem. Res. 1980, 13, 426-432.
- Blakemore, D. C.; Gilbert, A. J. Chem. Soc., Perkin Trans. 1 1992, 2265.
- Bryce-Smith, D.; Foulger, B.; Forrester, J.; Gilbert, A.; Orger, B. H.; Tyrrell, H. M. J. Chem. Soc., Perkin Trans. 1 1980, 55–71.
- 11. Krauch, C. H.; Kuster, H. Chem. Ber. 1964, 97, 2085-2086.
- 12. Hoffmann, H. M. R. Angew. Chem., Int. Ed. Engl. 1969, 8, 556–577.
- 13. Epiotis, N. D. *Theory of Organic Reactions*; Springer: New York, 1978; pp 150–152.
- 14. Bailey, W. J.; Baylouny, R. A. J. Org. Chem. 1962, 27, 3476–3478.
- Brinker, U. H.; Fleischhauer, I. Angew. Chem., Int. Ed. Engl. 1979, 18, 396–397.
- 16. Scott, L. T.; Erden, I. J. Am. Chem. Soc. 1982, 104, 1147–1149.
- Hasselmann, D.; Loosen, K. Angew. Chem., Int. Ed. Engl. 1978, 17, 606–608.
- 18. Kopecky, K. R.; Lau, M.-P. J. Org. Chem. 1978, 43, 525-526.
- Pryor, W. A.; Graham, W. D.; Green, J. G. J. Org. Chem. 1978, 43, 526–528.
- Gajewski, J. J.; Gortva, A. M. J. Am. Chem. Soc. 1982, 104, 334–335.
- 21. Bartmess, J. E. J. Am. Chem. Soc. 1982, 104, 335-337.
- 22. Scott, L. T.; Brunsvold, W. R. J. Org. Chem. 1979, 44, 641.
- 23. Gajewski, J. J.; Gortva, A. M. J. Org. Chem. 1989, 54, 373–378.
- 24. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Chemie: Weinheim, 1970.
- 25. Murata, I.; Nakazawa, T.; Kato, M.; Tatsuoka, T.; Sugihara, Y. *Tetrahedron Lett.* **1975**, 1647–1650.
- Nogaideli, A. I.; Tabashidze, N. I. J. Org. Chem. USSR (Eng. Trans.) 1969, 5, 717–718. Zh. Org. Khim. 1969, 5, 732–734.