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# PHOTOLYTIC GENERATION OF KETONES FROM 6-PHENANTHRIDINYLMETHYL ETHERS OF SECONDARY ALCOHOLS

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***Abstract:*** *Ketones are generated by photolysis (>320 nm) of 6-phenanthridinylmethyl ethers of secondary alcohols. The 6-phenanthridinylmethyl group may therefore be utilized as a latent carbonyl function, especially as the 6-phenanthridinyl-methyl group is chemically inert toward hydroboration, Grignard additions, $LiAlH_4$-reduction, bromination or ozonolysis at other parts of the molecule.*

Stermitz had shown [1] that the photolysis of the 2-quinolinylmethyl ether **2a** led to quinaldine (**4**) and formaldehyde (**3a**). Based on this observation we studied [2] the potential of quinaldyl ethers **2b** of secondary alcohols as protective groups with the aim to convert the "protected alcohols" at a later stage directly into ketones **3b**. On photolysis of various derivatives **2b** the desired ketones **3b** were indeed obtained [2]. Yet, aside from the generation of t-butylcyclohexanone (85% yield), the yields were generally only moderate, especially if the ketones formed were α-branched. Therefore, the use of quinaldine ethers **2b** as latent carbonyl functions met with only limited success. The decrease in the yields of the ketone was traced to a secondary photodecomposition of the ketones **3b** by the actinic light. The absorption of the quinaldine ethers **2b** does not reach beyond 320 nm and prevented the use of light of longer wavelength for this process. Since this photocleavage originates from an excited singlet state [1,3], use of sensitisers which could be excited at longer wavelength was precluded as well. One way out of this dilemma is, to use modified protecting groups which absorb at longer wavelengths. An obvious choice are the 6-phenanthiridinylmethyl ethers **5**.

### *Generation and Chemical Stability of 6-Phenanthridinylmethyl Ethers of Secondary Alcohols*

The preparation of the phenanthridinylmethyl ethers **5** started from the known 6-chloromethylphenanthridine (**7**) [4], which was converted to the more reactive 6-bromomethyl compound **8**. The latter was used to convert 4-t-butylcyclohexanol, as well as 2-methyl-6-hepten-3-ol into the phenanthridinylmethyl ethers.

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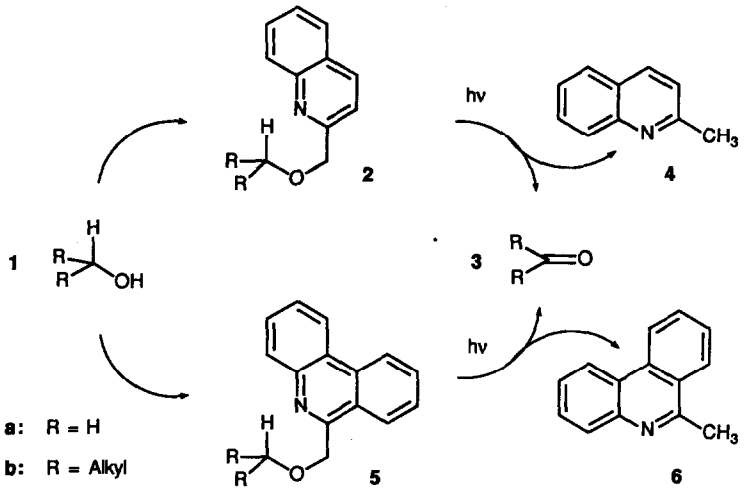
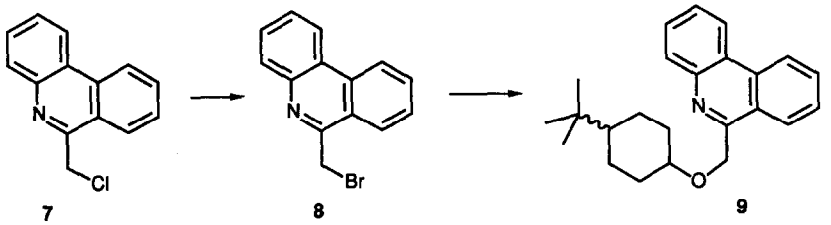
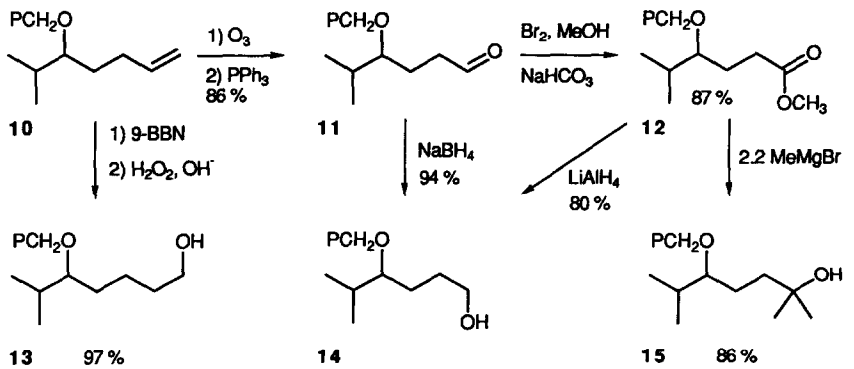
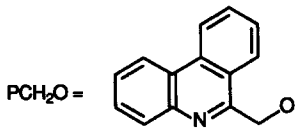



It was noted that the standard procedure for ether formation, NaH in refluxing THF led to partial decomposition of **8**, which limited the yields of the ethers **9** and **10** (62 and 67%). We did not attempt to improve the ether formation at this stage.



We tested rather first, whether the 6-phenanthridinylmethyl group is sufficiently chemically inert, to be used as a long term protective group during multistage syntheses. For this reason we carried out several representative transformations starting with the ether **10**. It was found that the 6-phenanthridinylmethyl group stands up quite well to oxidative conditions (ozone or bromine), to reducing conditions ($NaBH_4$, $LiAlH_4$), as well as to hydroboration or Grignard additions. The 6-phenanthridinylmethyl group therefore fulfils the requirements for a long term protective group.





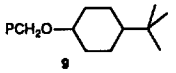
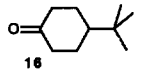
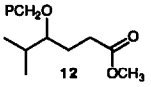
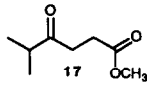
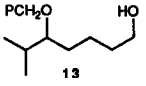
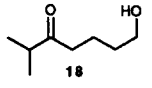
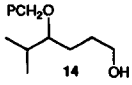
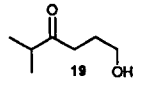

***Photolytic Conversion of 6-Phenanthridinylmethyl Ethers into Ketones***

The point of interest is the efficiency by which such 6-phenanthridinylmethyl ethers can be converted to ketones. 4 h radiation of **9** in acetonitrile through a Duran glass filter gave t-butylcyclohexanone **16** in 93% yield alongside with 6-methylphenanthridine (**6**) (100%). Thus, the 6-phenanthridinylmethyl group is in fact superior to the 2-quinolinylmethyl derivatives studied previously [2]. When a double layer of Duran glass was used as a filter, the photolysis rate became expectedly slower. The results of photocleavage experiments on various others 6-phenanthridinylmethyl ethers are compiled in the following table.

Probably higher conversions could be attained by longer irradiation times. But even with the limited photolysis time of 10 h were the yields and the product selectivities higher than on photolysis of the previously studied 2-quinolinylmethyl ethers **2**. The photolysis reaction became cleaner on irradiation at lower temperatures, cf. entry 3 of the table. It is therefore likely, that the photolyses of the 6-phenanthridinylmethyl ethers **5** to give the ketones **3** could be further optimized by application of a better light filter system and of lower temperatures. Ketone-yields approaching 90% may be expected with such systems.

We conclude that the 6-phenanthridinylmethyl ethers **5** fulfil all the requirements to be used as a protective group and as a latent carbonyl function in organic synthesis. The 6-phenanthridinylmethyl ethers should be added to the list of alcohol derivatives [5] that are available for this purpose.

**Table:** Irradiation of the 6-Phenanthridinylmethyl Ethers

| Entry | Starting Ethers | Irradiation time (h) | Ketones | 6-$CH_3$-Phenanthridine (6) | Starting Material recovered |
|---|---|---|---|---|---|
| 1 |  9 | 4 a) | 93 %  16 | 100 % | -- |
| 2 |  12 | 10 b) | 68 %  17 | 83 % | 2 % |
| 3 | | 10 b) c) | 67 % | 75 % | 14 % |
| 4 |  13 | 12 b) | 66 %  18 | 73 % | 5 % |
| 5 |  14 | 10 b) | 66 %  19 | 76 % | 3 % |

a) Single layer of Duran glass; b) Double layer of Duran glass; c) Photolysis at -10 to -20°C.

## EXPERIMENTAL

All temperatures quoted are not corrected. - $^1$H NMR and $^{13}$C NMR: Bruker AM 300. - Column chromatography: Kieselgel 60 (230 - 400 mesh, Merck, Darmstadt). - Photolyses: Heraeus medium pressure mercury lamp Q 180.

1. 6-Bromomethylphenanthridine (**8**): To a solution of 4.20 g (18.5 mmol) of 6-chloromethylphenanthridine (**7**) [4] in 150 ml of THF was added 16.50 g (0.19 mol) of lithium bromide under argon. After refluxing for 7 h, 50 ml of water were added, the organic phase was separated an the aqueous phase was extracted twice with 100 ml of ether each. The combined organic extracts were dried with $Na_2SO_4$ and concentrated. The crude product obtained was recrystallized from methanol to give a quantitative yield of **8** as a yellow solid of m.p. 135 - 137 °C. - $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 5.08 (s, 2H), 7.63 - 7.78 (m, 3H), 7.82 - 7.90 (m, 1H), 8.14 (dd, $J$ = 1.5 and 8.0 Hz, 1H), 8.35 (d, $J$ = 7.6 Hz, 1H), 8.55 (dd, $J$ = 1.5 and 8.0 Hz, 1H), 8.66 (d, $J$ = 8.4 Hz, 1H). - $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 32.0, 122.2, 122.7, 124.3, 124.5, 126.5, 127.6, 127.8, 129.1, 130.3, 131.0, 133.5, 143.4, 156.0. $C_{14}H_{10}BrN$ (272.2) Calcd. C 61.79 H 3.70 N 5.15. Found C 61.17 H 3.64 N 4.99 %.

2. 4-t-Butyl-cyclohexyl 6-phenanthridinylmethyl ether (**9**): A flask was charged with 0.79 g (2.9 mmol) of 6-bromomethylphenanthridine (**8**) and 90 mg (3.8 mmol) of sodium hydride. The flask was purged with nitrogen and 40 ml of THF was added. The mixture was heated to reflux under stirring and a solution of 0.40 g (2.6 mmol) of 4-t-butylcyclohexanol (1:2 cis/trans-mixture) in 10 ml of THF was added dropwise. After 6 h reflux the cold mixture was hydrolyzed by dropwise addition of water. The phases were separated, and the aqueous phase was extracted twice with 20 ml each of ether. The combined organic extracts were washed with 20 ml of brine, dried with $Na_2SO_4$ and concentrated. The residue was purified by chromatography using petroleum ether/ether = 4:1 to give 0.55 g (62%) of **9** (40:60 cis/trans mixture) as a colorless oil. - $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.78, 0.81 (2s, 9H), 0.90 - 1.00 (m, 2H), 1.12 - 1.50 (m, 4H), 1.73 - 1.76 (m, 1H), 2.04 (d, $J$ = 11.4 Hz, 1H), 2.15 (d, $J$ = 11.2 Hz, 1H), 3.34 - 3.45 (m, 0.7H), 3.78 (broad s, 0.3H), 5.08 (s, 0.8H), 5.15 (s, 1.2H), 7.56 - 7.72 (m, 3H), 7.74 - 7.81 (m, 1H), 8.10 - 8.17 (m, 1H), 8.46 (d, $J$ = 9.4 Hz, 1H), 8.50 (d, $J$ = 9.1 Hz, 1H), 8.57 (d, $J$ = 8.3 Hz, 1H). - $^{13}$C NMR (75 MHz, $CDCl_3$): cis-isomer: $\delta$ = 21.6, 27.5, 32.3, 32.6, 47.9, 72.4, 73.9, 122.1, 124.4, 125.5, 127.1, 127.2, 127.3, 127.4, 127.7, 130.1, 130.5, 133.2, 143.3, 158.6; trans-isomer: $\delta$ = 25.7, 27.7, 30.6, 32.8, 47.5, 72.0, 78.8, 122.0, 124.2, 125.4, 125.5, 127.1, 127.2, 127.3, 127.4, 128.6, 130.2, 130.5, 133.2, 143.3, 158.2. $C_{24}H_{29}NO$ (347.5) Calcd. C 82.95 H 8.41 N 4.03. Found C 82.94 H 8.64 N 3.94%.

3. 6-Methyl-5-(6-phenanthridinylmethoxy)-1-heptene (**10**): 1.38 g (5.1 mmol) of 6-bromomethylphenanthridine (**8**), 160 mg (6.7 mmol) of sodium hydride, and 0.50 g (1.3 mmol) of 5-hydroxy-6-methyl-1-heptene were allowed to react as described under 2. Chromatography with petroleum ether/ether = 7:3 furnished 0.92 g (67%) of **10** as a colorless oil. - $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.81 (d, $J$ = 6.9 Hz, 3H), 0.83 (d, $J$ = 6.9 Hz, 3H), 1.47 - 1.60 (m, 2H), 1.86 - 2.14 (m, 3H), 3.33 (dt, $J$ = 6.9 and 9.5 Hz, 1H), 4.78 - 4.88 (m, 2H), 5.07 (d, $J$ = 11.4 Hz, 1H), 5.13 (d, $J$ = 11.4 Hz, 1H), 5.68 (ddt, $J$ = 17.0, 10.3, and 6.6 Hz, 1H), 7.58 - 7.72 (m, 3H), 7.74 - 8.00 (m, 1H), 8.12 (dd, $J$ = 8.0 and 1.4 Hz, 1H), 8.45 (d, $J$ = 8.0 Hz, 1H), 8.49 (dd, $J$ = 8.1 and 3.6 Hz, 1H), 8.56 (d, $J$ = 8.5 Hz, 1H). - $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 17.5, 18.4, 29.0, 29.7, 29.9, 73.0, 84.0, 114.3, 121.9, 122.0, 124.4, 125.4, 127.0, 127.1, 127.5, 128.5, 130.1, 130.4, 133.1 138.7, 143.3, 158.1. $C_{22}H_{25}NO$ (319.5) Calcd. C 82.72 H 7.89 N 4.38. Found C 82.44 H 7.83 N 4.27 %.

4. 5-Methyl-4-(2-phenanthridinylmethoxy)hexanal (**11**): In a solution of 0.60 g (1.9 mmol) of 6-methyl-5-(2-phenanthridinylmethoxy)-1-heptene (**10**) in 20 ml of dichloromethane was introduced at -78°C a stream of ozone until TLC indicated complete consumption of the olefin. Excess of ozone was purged with a stream of nitrogen. 0.70 g (2.7 mmol) of triphenylphosphine were added and the mixture was stirred for 3.5 h at room temperature. The solvents were removed i.vac. and the residue was chromatographed using petroleum ether/ether = 3:7 to give 0.51 g (88%) of **11** as a colorless oil. - $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.84 (d, $J$ = 6.9 Hz, 3H), 0.86 (d, $J$ = 6.9 Hz, 3H), 1.65 - 1.87 (m, 2H), 2.00 (quit., $J$ = 6.8 Hz, 1H), 2.25 - 2.47 (m, 2H), 3.32 - 3.49 (m, 1H), 5.03 (d, $J$ = 11.6 Hz, 1H), 5.17 (d, $J$ = 11.6 Hz, 1H), 7.60 - 7.74 (m, 3H), 7.78 - 7.86 (m, 1H), 8.13 (dd, $J$ = 8.0 and 1.6 Hz, 1H), 8.39 (d, $J$ = 8.3 Hz, 1H), 8.53 (dd, $J$ = 8.0 and 1.6 Hz, 1H), 8.6 (d, $J$ = 8.4 Hz, 1H), 9.58 (t, $J$ = 1.5 Hz, 1H). - $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 17.1, 18.8, 22.0, 30.0, 40.2, 72.9, 83.8, 122.1, 122.3, 124.1, 125.1, 127.2, 127.3, 128.7, 130.2, 130.7, 134.1, 143.0, 157.8, 202.6.

5. Methyl 5-methyl-4-(6-phenanthridinylmethoxy)hexanoate (**12**): A solution of 0.67 g (2.1 mmol) of 5-methyl-4-(6-phenanthridinylmethoxy)hexanal (**11**) in 10 ml of methanol and 1 ml of water was buffered by addition of 3.37 g (0.04 mol) of sodium hydrogencarbonate. 4.5 ml of a 2 M solution of bromine in methanol/water (9:1) was added dropwise. After stirring for 15 min, the excess of bromine was decolorized by addition of sodium thiosulfate. 100 ml of water were added and the mixture was extracted three times with 20 ml each of ether. The combined organic phases were dried with $Na_2SO_4$ and concentrated. Chromatography with petroleum ether/ether = 1:1 furnished 0.63 g (87%) of the ester **12** as a colorless oil. - UV ($CH_3CN$) $\lambda_{max}$ (log $\epsilon$) = 343 (3.3), 328 (3.7), 300 (3.65), 286 (3.76), 272 (3.96), 248 (4.67). - $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 0.84 (d, $J$ = 6.8 Hz, 3H), 0.85 (d, $J$ = 6.8 Hz, 3H), 1.62 - 1.88 (m, 2H), 2.01 (quint., $J$ = 6.8 Hz, 1H), 2.15 - 2.36 (m, 2H), 3.31 - 3.38 (m, 1H), 3.47 (s, 3H), 5.04 (d, $J$ = 11.5 Hz, 1H), 5.16 (d, $J$ = 11.5 Hz, 1H), 7.58 - 7.72 (m, 3H), 7.78 - 7.84 (m, 1H), 8.12 (dd, $J$ = 8.0 and 1.4 Hz, 1H), 8.42 (d, $J$ = 8.1 Hz, 1H), 8.53 (dd, $J$ = 8.0 and 1.4 Hz, 1H), 8.60 (d, $J$ = 8.0 Hz, 1H). - $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 17.1, 18.6, 24.8, 29.8, 30.1, 51.3, 72.8, 83.6, 121.9, 122.1, 124.3, 125.2, 127.0, 127.2, 127.3, 128.5, 130.1, 130.5, 133.0, 144.0, 157.8, 174.2. $C_{22}H_{55}NO_3$ (351.5) Calcd. C 75.19 H 7.17 N 3.99. Found C 75.25 H 7.15 N 4.01 %.

6. 6-Methyl-5-(6-phenanthridinylmethoxy)-1-heptanol (**13**): A solution of 335 mg (1.05 mmol) of 6-methyl-5-(6-phenanthridinylmethoxy)-1-heptene (**10**) in 3 ml of THF was added to 3.2 ml of a 0.5 M solution of 9-borabicyclo[3.3.3]nonane in THF at room temperature. After 1 h 3.3 ml of ethanol, 1.65 ml of 6 N aqueous sodium hydroxide solution and 1.65 ml of 30% aqueous hydrogen peroxide were added. The mixture was heated for 1 h to 50°C, the aqueous phase was saturated with solid potassium carbonate. The organic phase was separated and the aqueous phase was extracted twice with 20 ml each of ether. The combined organic phases were dried with $Na_2SO_4$ and concentrated. Chromatography with ether furnished 342 mg (97%) of **13** as a colorless oil. - $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 0.85 (d, $J$ = 7.2 Hz, 3H), 0.89 (d, $J$ = 7.2 Hz, 3H), 1.20 - 1.60 (m, 6H), 1.77 (broad s, 1H), 1.98 (quint., $J$ = 7.0 Hz, 1H), 3.30 - 3.37 (m, 1H), 3.50 (t, $J$ = 6.1 Hz, 2H), 5.09 (d, $J$ = 11.4 Hz, 1H), 5.21 (d, $J$ = 11.4 Hz, 1H), 7.62 - 7.76 (m, 3H), 7.81 - 7.87 (m, 1H), 8.17 (d, $J$ = 7.8 Hz, 1H), 8.49 (d, $J$ = 8.2 Hz, 1H), 8.56 (d, $J$ = 7.9 Hz, 1H), 8.62 (d, $J$ = 8.2 Hz, 1H). - $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 17.9, 18.5, 21.6, 29.4, 30.3, 32.7, 62.7, 72.8, 77.2, 84.6, 122.0, 122.1, 124.4, 125.5, 127.1, 127.2, 127.6, 128.6, 130.0, 130.6, 144.8, 158.2. $C_{22}H_{27}NO_2$ (337.5) Calcd. C 78.30 H 8.06 N 4.15. Found C 78.21 H 8.12 N 3.95 %.

7. 5-Methyl-4-(6-phenanthridinylmethoxy)-1-hexanol (**14**): To a suspension of 16.5 mg (0.43 mmol) of lithium aluminium hydride in 5 ml of THF was added a solution of 102 mg (0.29 mmol) of methyl 5-methyl-4-(6-phenanthridinylmethoxy)hexanoate (**12**) in 2 ml of THF at 0°C. After stirring for 30 min at room temperature 2 ml of water and subsequently 30 ml of 2 N aqueous sodium hydroxide solution were added. The mixture was stirred for 20 min and filtered through Celite. The Celite was washed thoroughly with ether and the combined organic phases were dried with $Na_2SO_4$ and concentrated. Chromatography with ether furnished 75 mg (80%) of **14** as a colorless oil. - $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 0.88 (d, $J$ = 6.8 Hz, 3H), 0.92 (d, $J$ = 6.8 Hz, 3H), 1.56 - 1.74 (m, 4H), 2.03 (quint., $J$ = 6.7 Hz, 1H), 2.56 (broad s, 1H), 3.37 - 3.42 (m, 1H), 3.54 - 3.68 (m, 2H), 5.14 (d, $J$ = 11.7 Hz, 1H), 5.28 (d, $J$ = 11.7 Hz, 1H), 7.65 - 7.79 (m, 3H), 7.82 - 7.91 (m, 1H), 8.21 (d, $J$ = 7.7 Hz, 1H), 8.47 (d, $J$ = 8.2 Hz, 1H), 8.58 (d, $J$ = 7.9 Hz, 1H), 8.66 (d, $J$ = 8.2 Hz, 1H). - $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 17.7, 18.6, 25.7, 28.6, 30.1, 62.5, 72.2, 84.6, 121.9, 122.1, 124.3, 125.2, 127.0, 127.1, 127.2, 128.6, 130.0, 130.6, 133.1, 143.2, 157.9. $C_{21}H_{25}NO_2$ (323.4) Calcd. C 77.98 H 7.79 N 4.33. Found C 78.11 H 7.82 N 4.31 %.

8. 1,1,5-Trimethyl-4-(6-phenanthridinylmethoxy)-1-hexanol (**15**): To a solution of 95 mg (0.27 mmol) of methyl 5-methyl-4-(6-phenanthridinylmethoxy)hexanoate (**12**) in 10 ml of ether was added at 0°C 0.22 ml of a 2.72 M solution of methylmagnesium bromide in ether. After stirring for 30 min 10 ml of saturated aqueous $NH_4Cl$-solution was added. The phases were separated and the aqueous phase was extracted twice with 10 ml of ether. The combined organic phases were dried with $Na_2SO_4$ and concentrated. Chromatography with ether furnished 82 mg (86%) of **15** as a colorless oil. - $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 0.82 (d, $J$ = 6.8 Hz, 3H), 0.85 (d, $J$ = 6.8 Hz, 3H), 1.05 (s, 3H), 1.06 (s, 3H), 1.26 - 1.50 (m, 2H), 1.52 - 1.64 (m, 2H), 1.91 (quint., $J$ = 6.8 Hz, 1H), 2.02 (broad s, 1H), 3.28 (q, $J$ = 5.9 Hz, 1H), 5.05 (d, $J$ = 11.5 Hz, 1H), 5.15 (d, $J$ = 11.5 Hz, 1H), 7.56 - 7.70 (m, 3H), 7.72 - 7.80 (m, 1H), 8.13 (dd, $J$ = 8.1 and 1.3 Hz, 1H), 8.42 (d, $J$ = 8.4 Hz, 1H), 8.48 (dd, $J$ = 8.0 and 1.5 Hz, 1H), 8.55 (d, $J$ = 8.1 Hz, 1H). - $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 17.8, 18.6, 23.9, 28.9, 29.3, 30.2, 38.9, 70.4, 72.3, 84.9, 121.8, 122.0, 124.2, 125.3, 127.0, 127.1, 127.4, 128.5, 130.0, 130.4, 133.0, 143.1, 158.0. $C_{23}H_{29}NO_2$ (351.5) Calcd. C 78.59 H 8.32 N 3.99. Found C 78.11 H 8.50 N 4.07 %.

9. 4-t-Butylcyclohexanone (**16**): A solution of 194 mg (0.56 mmol) of 4-t-butylcyclohexyl (6-phenanthridinylmethyl) ether (**9**) in 70 ml of acetonitrile was flushed with argon for 30 min. The solution was irradiated with a medium pressure mercury lamp in an immersion reactor through a single layer of Duran glass. The progress of the reaction was monitored by TLC. After 4 h the solution was concentrated and the residue was chromatographed with chloroform to give 80.5 mg (93 %) of **16** as a colorless solid. **16** was identified by comparison of its m.p. and the NMR-spectra with a commerical sample. Further elution provided 108 mg (100%) of 6-methylphenanthridine (**6**): $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.93 (s, 3H), 7.49 (dd, $J$ = 8.2 and 1.2 Hz, 1H), 7.55 (dd, $J$ = 8.2 and 1.2 Hz, 2H), 7.60 - 7.77 (m, 2H), 8.04 (d, $J$ = 8.2 Hz, 1H), 8.05 (dd, $J$ = 8.2 and 1.2 Hz, 1H), 8.38 (dd, $J$ = 8.2 and 1.3 Hz, 1H), 8.44 (d, $J$ = 8.0 Hz, 1H). - $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 23.4, 122.0, 122.3, 123.8, 125.9, 126.4, 126.5, 127.3, 128.7, 129.4, 130.5, 132.5, 143.8, 158.9.

10. Methyl 5-methyl-4-oxohexanoate (**17**): A solution of 302 mg (0.86 mmol) of methyl 5-methyl-4-(6-phenanthridinylmethoxy)hexanoate (**12**) was irradiated in 110 ml of acetonitrile through a double layer of Duran glass as described under 9. Chromatography of the crude product with petroleum ether/ether = 2:1 furnished 92 mg of the ketoester **17** [6] as a colorless oil. The material was identical to a sample obtained in ref. [2]. Further elution furnished 38 mg (83%) of 6-methylphenanthridine (**6**) and 5 mg (1.6 %) of recovered starting material.

11. 2-Methyl-7-hydroxy-3-heptanone (**18**): A solution of 285 mg (0.84 mmol) of 6-methyl-5-(6-phenanthridinyl-methoxy)-1-heptanone (**13**) in 105 ml acetonitrile was irradiated for 12 h as described under 10. Chromatography of the crude product with petroleum ether/ether = 3:7 gave 80 mg (66%) of **18** [7] as a colorless oil. The material was identical to a sample obtained in ref. [2]. Further elution furnished 120 mg (73%) of 6-methylphenanthridine (**6**) and 15 mg (5%) of recovered starting material.

12. 2-Methyl-6-hydroxy-3-hexanone (**19**): A solution of 310 mg (0.96 mmol) of 5-methyl-4-(6-phenanthridinyl-methoxy)-1-hexanol (**14**) in 120 ml of acetonitrile was irradiated for 10 h as described under 10. Chromatography with petroleum ether/ether = 1:4 furnished 82 mg (66 %) of **19** [8] as a colorless oil. The material was identified with reference to a sample obtained under ref. [2]. Further elution furnished 140 mg (76%) of 6-methylphenanthridine (**6**) and 17 mg (3%) of recovered starting material.

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## REFERENCES AND NOTES

1. Stermitz, F.R.; Wei, C.C.; O'Donnell, C.M., *J. Am. Chem. Soc.* **1970**, *92*, 2745.
2. Rukachaisirikul, V.; Koert, U.; Hoffmann, R. W. *Tetrahedron* **1992**, *48*, 4533-4544.
3. Prathapan, S.; Loft, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 3940.
4. Morgan, G. T.; Walls, L. P. *J. Chem. Soc. London,* **1931**, 2447.
5. a) Curran, D. P.; Yu, H. *Synthesis* **1992**, 123; b) Tolstikov, G. A.; Miftakhov, M. S.; Vostrikov, N. S.; Komissarova, N. G.; Adler, M. E.; Kuznetsov, O. M. *Zh. Org. Khim.* **1988**, *24*, 224; c) Mahrwald, R.; Theil, F.; Schick, H.; Palme, H.-J.; Nowack, H.; Weber, G.; Schwarz, S. *Synthesis* **1987**, 1012; d) Baker, R.; Rao, V. B.; Ravenscroft, P. D.; Swain, C. J. *Synthesis* **1983**, 572; e) Olah, G. A.; Gupta, B. G. B.; Fung, A. P. *Synthesis* **1980**, 897; f) Olah, G. A.; Ho, T.-L. *Synthesis* **1976**, 609; g) Jung, M. E. *J. Org. Chem.* **1976**, *41*, 1479.
6. Kunkel, E.; Reichelt, I.; Reißig, H.-U. *Liebigs Ann. Chem.* **1984**, 802.
7. Nikishin, G. I.; Kapustina, N. I.; Lubuzh, E. D.; Spektor, S. S.; Kaplan, E. P. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1980**, *11*, 2607; *Chem. Abstr.* **1981**, *94*, 191617e.
8. Fuji, K.; Node, M.; Usami, Y. *Chem. Lett.* **1986**, 961.