

The Chemistry of Polycyclic Arene Imines. II.  
Photochemistry of Phenanthrene 9,10-Imine and of Its  
*N*-Butyl Derivative [1] [2]

Moshe Weitzberg, David Avnir, Zeev Aizenshtat and Jochanan Blum\*

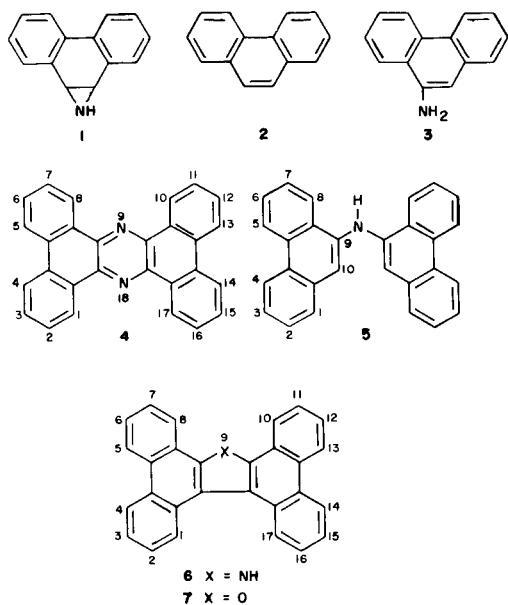
Department of Organic Chemistry, The Hebrew University, Jerusalem  
91904, Israel

Received December 7, 1982

The uv irradiation of phenanthrene 9,10-imine has been shown to give 9*H*-tetrabenzo[*a,c,g,i*]carbazole as the major photo-product both in argon purged acetone and in dichloromethane. Phenanthrazine, *N*-9-phenanthrenyl-9-phenanthrenamine and phenanthrene were formed in smaller quantities. 9-Phenanthrenamine was found to be a minor by-product. *N*-Butylphenanthrene 9,10-imine yielded under similar conditions phenanthrene and *N*-butyl-9-phenanthrenamine as the only isolable polycyclic compounds. In the presence of air the substituted imine gave mainly 2-propylphenanthro[9,10-*d*]oxazole.

*J. Heterocyclic Chem.*, **20**, 1019 (1983).

While the photochemistry of polycyclic arene oxides has been the focus of substantial research [3], only one of a light-induced transformation of an arene imine has been announced [4]. In this paper we report the first detailed study on the photochemical transformations of two phenanthrene imine derivatives.



By analogy to the photochemistry of both arene oxides, that give phenols, ketones and oxepine derivatives [3], and aliphatic aziridines in which C—C bonds are cleaved homolytically [5], we expect the main photo-products of the title compounds to be phenanthrenamines and dibenzazepines. In fact, photolysis of 1*a*,9*b*-dihydro-1*H*-phenanthro[9,10-*b*]azirine (phenanthrene 9,10-imine) (**1**) by a medium pressure mercury lamp gave in argon-purged dichloromethane as well as in acetone five isolable solid compounds **2-6**, none of which was an azepine derivative. 9*H*-Tetrabenzo[*a,c,g,i*]carbazole (**6**) was the major product

regardless of the nature of the solvent and changes in accord with the filter employed. Two other "dimeric" compounds were phenanthrazine (**4**) and *N*-9-phenanthrenyl-9-phenanthrenamine (**5**). Phenanthrene itself (**2**) was formed in considerable quantities, but the yield of 9-phenanthrenamine (**3**) was very small. Ammonia was the only detectable gas formed during the irradiation.

The results of some typical irradiations of **1** are summarized in Table I.

Table I

Photochemical Transformation of Phenanthrene 9,10-Imine (**1**) (a)

Exp.	Reaction conditions (b)	Yield of product (%) (c)				
		<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
1	Ac, P	3.6	0.9	6.8	8.6	22.2
2	Mc, Q	7.5	2.9	14.6	5.8	19.1
3	Ac, P, Phen	N.A.	0.4	0.9	11.6	28.0

(a) The irradiation was discontinued after 40% conversion (1-2 hours in experiments 1 and 2; 4-5 hours in experiment 3). (b) Ac - acetone; Mc - dichloromethane; P - Pyrex filter; Q - quartz well; Phen - 0.15 equivalent of phenanthrene was added to the reaction mixture per each equivalent of **1**. (c) Calculated for reacted imine.

The structures of compounds **2-4** were established by direct comparison with authentic samples. *N*-9-Phenanthrenyl-9-phenanthrenamine (**5**) that proved to have completely different properties than that reported by Schmidt and Lumpf [6] and the carbazole derivative **6** that had not been reported before, were compared with samples prepared by oxidative coupling of 9-phenanthrenamine (**3**) at 260° in the presence of iodine. The 300 MHz pmr spectra of **5** and **6** were found to be particularly indicative. In **5** the H-10 and H-10' protons show up as a distinguished singlet at 7.195 ppm (see Experimental). The pmr spectrum of **6** resembles closely that of the isoelectronic diphenanthro[9,10-*b*:9',10'-*d*]furan (**7**) [7] (See Table II).

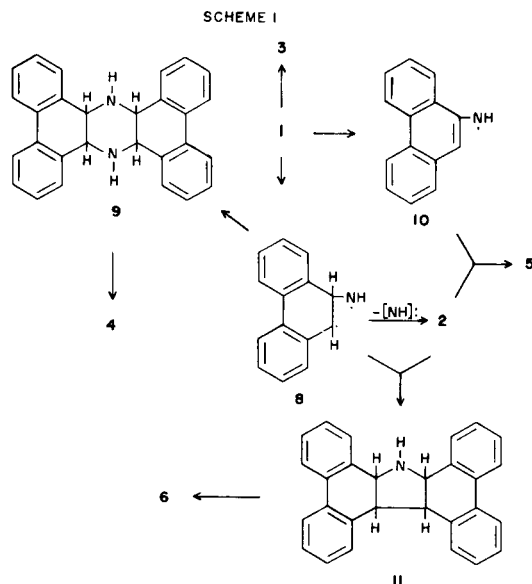
Table II

300 MHz pmr Data of 9*H*-Tetrabenz[*a,c,g,i*]carbazole (**6**) and of Diphenanthro[9,10-*b*:9',10'-*d'*]furan (**7**)

Assigned protons	Chemical Shifts ( $\delta$ , ppm) and Coupling Constants (Hz)	
	<b>6</b> (a)	<b>7</b> (b)
H-1, H-17	8.926 (c) (d, $J_{1,2} = 8.1$ )	8.788 (d, $J_{1,2} = 7.5$ )
H-2, H-16	7.713 (dd, $J_{1,2} = J_{2,3} = 8.1$ )	7.757 (dd, $J_{1,2} = J_{2,3} = 7.5$ )
H-3, H-15	7.745 (dd, $J_{2,3} = J_{3,4} = 8.1$ )	7.784 (dd, $J_{2,3} = J_{3,4} = 7.5$ )
H-4, H-14	9.108 (d, $J_{3,4} = 8.1$ )	9.107 (d, $J_{3,4} = 7.5$ )
H-5, H-13	8.926 (c) (d, $J_{5,6} = 8.1$ )	8.851 (d, $J_{5,6} = 8.0$ )
H-6, H-12	7.659 (dd, $J_{5,6} = J_{6,7} = 8.1$ )	7.728 (dd, $J_{5,6} = 8.0$ ; $J_{6,7} = 7.5$ )
H-7, H-11	7.772 (dd, $J_{6,7} = J_{7,8} = 8.1$ )	7.808 (d, $J_{6,7} = J_{7,8} = 7.5$ )
H-8, H-10	8.755 (d, $J_{7,8} = 8.1$ )	8.668 (d, $J_{7,8} = 7.5$ )
H-9	7.683 (s)	—

(a) In hexadeuterioacetone. (b) In deuteriochloroform. (c) Superimposed peaks.

While the nature of the solvent and the wave length of the irradiated light proved to have only a little effect on the yields of **5** and **6** and a moderate influence on the formation of **4** (see Table I), the addition of a small amount of phenanthrene (0.15 equivalent per each equivalent of **1** caused an increase in the yields of **5** and **6** and a very significant decrease in the formation of **4**. This observation can be explained in light of the proposed reaction mechanism shown in Scheme I.



We assume that **1** undergoes reversible C—N bond cleavage with the formation of the biradical **8**. This species may, in turn lose nitrene to give phenanthrene (**2**). The biradical may also undergo dimerization and yield 1*b*,8*b*,9,9*a*,17*b*,18-hexahydrophenanthrazine (**9**) followed by oxidation (by free radical or nitrene) to form **4**.

Photolytic disproportionation of **1** or hydrogen abstraction from the starting imine should give radical **10**. Combination of **10** with **2** gives the *N*-9-phenanthrenyl-9-phenanthrenamine (**5**). Likewise, the reaction of **8** with **2** should form the precursor of **6** — 9*H*-8*b*,9*a*,12*b*,12*c*-tetrahydrobenzo[*a,c,g,i*]carbazole (**11**). Thus, addition of phenanthrene to the reaction mixture enhances the consumption of **8** and decreases its chances to dimerize.

Although all attempts to trace the intermediates **9** and **11** by mass-spectrometric measurements were unsuccessful, we found that during the initial stages of the reaction some labile compounds were formed. These compounds show transient resonance bands between 2 and 3.5 ppm in the pmr spectra and turn readily into **4** and **6** upon exposure to air.

It is noteworthy that none of the photoproducts result from the rearranged starting material — 9-phenanthrenamine (**3**). We have shown that under our experimental conditions, **3** is completely refractory to uv-irradiation. We have also proven that, in contrast to diphenylamine [8], **5** does not undergo any photochemical transformations. Thus, **6** cannot be formed by photocyclization of *N*-9-phenanthrenyl-9-phenanthrenamine.

Unlike the unsubstituted imine **1**, irradiation of 1-butyl-1*a*,9*b*-dihydro-1*H*-phenanthro[9,10-*b*]azirine (*N*-butylphenanthrene 9,10-imine) (**12**) [9] gave no isolable hexa- or hepta-cyclic products. Under an inert atmosphere the *N*-substituted imine yielded only phenanthrene (**2**) and *N*-butyl-9-phenanthrenamine (**13**) [10]. In the presence of air, a third compound, 2-propylphenanthro[9,10-*d*]oxazole (**14**) was obtained in substantial quantities. The formation of this product can be explained by interaction of oxygen with either **15** (*N*-butyl-analog of **8**) or with the rearranged [11] biradical **16**.

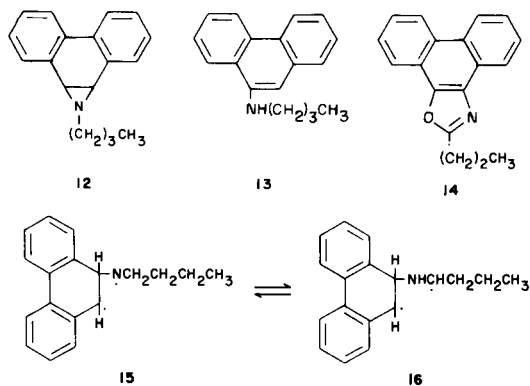
*N*-Butylamine was detected in the reaction mixture both under an ambient and under an Argon atmosphere.

The results of some irradiation of **12** are given in Table III.

Table III  
Photochemical Transformation of *N*-Butylphenanthrene 9,10-Imine (**12**) (a)

Product	Yield, (%) (b)		
	In argon purged dichloro-methane (c)	In dichloro-methane under air (c)	In acetone under air (d)
<b>2</b>	16.5	6.2	7.4
<b>13</b>	39.6	19.4	37.4
<b>14</b>	0.0	40.3	7.2

(a) The irradiation was discontinued after 90% of the starting material had reacted. For reaction conditions see Experimental. (b) Calculated for reacted imine. (c) The same results were obtained in quartz and Pyrex wells. (d) In a quartz well.



## EXPERIMENTAL

1a,9b-Dihydro-1*H*-phenanthro[9,10-*b*]azirine (1).

Following a new modification of our previous method [12], 12 ml of trimethyl phosphite was added to a solution of 5 g of *trans*-10-azido-9,10-dihydrophenanthren-9-ol [4] in 150 ml of dichloromethane. The mixture was refluxed for 3 hours, cooled and the solvent evaporated. Addition of a cold mixture of 95% ether and 5% hexane afforded the crude imine as colorless crystals. Flash chromatography [13] on silica gel with dichloromethane-hexane (4:1) as eluent, yielded 3 g (74%) of analytically pure **1**, mp 163-164° (lit [11] mp 163-164°).

Photolysis of **1**.

In a typical experiment 0.75 g of **1** in 200 ml of spectroscopical grade degassed dichloromethane was placed in a quartz tube (5 cm i.d.). The magnetically stirred solution was purged with argon and irradiated at room temperature with a 450 W medium pressure mercury lamp located at a distance of 10 cm from the reaction vessel. After 90 minutes, hplc analysis indicated 40% conversion. The irradiation was stopped and the reaction mixture divided into three equal portions. One portion was subjected to hplc analysis on an ALTECH R.P. 18 column with 90% aqueous methanol (flow rate 1.7 ml/minute). The starting material **1** (60%), phenanthrene (**2**) (8%) and 9-phenanthrenamine (**3**) (3%) [4] were eluted with 90% aqueous methanol and compared with authentic samples. The second portion was concentrated to a volume of 10 ml and left for 3 days in the refrigerator at -5°. The yellow precipitate (21.7 mg, 15%) proved to be pure phenanthrazine (**4**). Its physical properties were identical with those of the sample described below. In a second irradiation experiment this part of the reaction mixture was concentrated and chromatographed over a short column of silica gel (particle diameter 0.04-0.2 mm). The final fraction eluted with a mixture of 70% chloroform and 30% ethyl acetate proved to be pure **4**. The third portion was evaporated to dryness and 50 ml benzene added. A fast stream of dry hydrogen chloride was passed through the solution for one minute. The 9-phenanthrenamine hydrochloride was extracted with four portions of 50 ml of water. The organic solution was washed with 5% aqueous sodium bicarbonate and with water, dried (magnesium sulfate), concentrated and flash chromatographed [13] on silica gel with mixtures of hexane-ether (from pure hexane to a 1:1 mixture) as eluents. The initial fraction of 8.3 mg (6%) that was eluted with the highest percentage of ether proved to be pure *N*-9-phenanthrenyl-9-phenanthrenamine (**5**) having the same physical properties as the sample prepared from 9-phenanthrenamine (*vide infra*). The second fraction of 27.3 g (19%) obtained with the same eluent was pale yellow 9*H*-tetrabenzo[*a,c,g,i*]carbazole (**6**), mp 242-244°; ir (potassium bromide): 3460 cm<sup>-1</sup> (NH); uv (dichloromethane): λ max (log ε) 252 (4.93), 284 (sh) (4.41), 325 nm (4.23), 300 MHz pmr is given in Table II; ms: (70 eV, 200°) *m/e* 367 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>26</sub>H<sub>17</sub>N: C, 91.52; H, 4.66; N, 3.81. Found: C, 91.60; H, 4.76; N, 3.78.

Photolysis of **1** in acetone (AR grade) was conducted by a similar procedure in a Pyrex well. The results are summarized in Table I.

Phenanthrazine (**4**).

This compound was prepared according to Schiedt [14] by heating of 9,10-phenanthraquinone in formamide and acetic acid at 160°, mp >450° (from tetralin) (lit [14] mp 487°); 300 MHz pmr (pentadeuteriopyridine): 7.824 (ddd, J<sub>1,3</sub> = 1.5 Hz, J<sub>2,3</sub> = 7.1 Hz, J<sub>3,4</sub> = 8.1 Hz, H<sub>3</sub>, H<sub>6</sub>, H<sub>12</sub>, H<sub>15</sub>), 7.973 (ddd, J<sub>1,2</sub> = 8.2 Hz, J<sub>2,3</sub> = 7.1 Hz, J<sub>2,4</sub> = 1.0 Hz, H<sub>2</sub>, H<sub>7</sub>, H<sub>11</sub>, H<sub>16</sub>), 8.117 (dd, J<sub>1,3</sub> = 1.5 Hz, J<sub>1,2</sub> = 8.2 Hz, J<sub>1,3</sub> = 1.5 Hz, H<sub>1</sub>, H<sub>8</sub>, H<sub>10</sub>, H<sub>17</sub>), 8.300 (dd, J<sub>2,4</sub> = 1.0 Hz, J<sub>3,4</sub> = 8.1 Hz, H<sub>4</sub>, H<sub>5</sub>, H<sub>13</sub>, H<sub>14</sub>); ms: (70 eV, 200°) *m/e* 368 (M<sup>+</sup>).

Thermal Conversion of 9-Phenanthrenamine (**3**) into *N*-9-Phenanthrenyl-9-phenanthrenamine (**5**) and 9*H*-Tetrabenzo[*a,c,g,i*]carbazole (**6**).

A mixture of 1.6 g of 9-aminophenanthrene (**3**) [4] and 0.5 g iodine was heated with magnetic stirring at 260°. After 7 hours, the mixture was cooled and extracted into chloroform. The solution was washed first with aqueous sodium bicarbonate and sodium thiosulfate, then twice with water, three times with 5% hydrochloric acid and again with water and sodium bicarbonate. The chloroform solution was dried (magnesium sulfate) and evaporated. The residue (0.7 g) could be separated either by hplc on silica gel with a 1:1 mixture of ether-hexane as eluent, or by flash chromatography on silica with a mixture of 90% dichloromethane and 10% hexane. The first fractions yielded 0.45 g (29%) of **5** as colorless crystals of mp 228-229° (from ether) (lit [6] 370° [15]); ir: (potassium bromide): 3440 cm<sup>-1</sup> (NH); uv (dichloromethane): λ max (log ε) 254 (5.01), 325 nm (4.18); 300 MHz pmr (deuteriochloroform): 6.268 (br s 1H, NH), 7.195 (s, 2H, H<sub>10</sub>), 7.466-7.600 (m, 8H, H<sub>2</sub>, H<sub>6</sub>, H<sub>7</sub>, H<sub>8</sub>), 7.697 (ddd, 2H, J<sub>1,3</sub> = 1.5 Hz, J<sub>2,3</sub> = 5.9 Hz, J<sub>3,4</sub> = 8.8 Hz, H<sub>3</sub>), 8.197 (dd, 2H, J<sub>1,2</sub> = 8.1 Hz, J<sub>1,3</sub> = 1.5 Hz, H<sub>1</sub>), 8.642 (d, 2H, J<sub>5,6</sub> = 8.8 Hz, H<sub>5</sub>), 8.768 (dd, 2H, J<sub>2,4</sub> = 1.5 Hz, J<sub>3,4</sub> = 8.8 Hz, H<sub>4</sub>); ms: (70 eV, 70°) *m/e* (relative intensity) 369 (M<sup>+</sup>, 100), 368 [(M-H)<sup>+</sup>, 31], 367 [(M-2H)<sup>+</sup>, 29], 177 (C<sub>14</sub>H<sub>9</sub><sup>+</sup>, 6), 165 (C<sub>13</sub>H<sub>9</sub><sup>+</sup>, 7).

*Anal.* Calcd. for C<sub>28</sub>H<sub>19</sub>N: C, 91.03; H, 5.18; N, 3.79. Found: C, 90.92; H, 5.24; N, 3.97.

The final fractions that were eluted with the same mixture of solvents consisted of 0.15 g (10%) of **6** that was identical with the sample obtained by photolysis of **1**.

Almost identical results were obtained when the starting amine **3** was substituted by phenanthrene 9,10-imine **1** and the reaction mixture refluxed for 90 minutes.

Diphenanthro[9,10-*b*:9',10'-*d*]furan (**7**).

This compound was prepared in 10% yield from 9,10-phenanthraquinone according to Japp and Findlay [7], mp 305° (lit 306° [7]); the 300 MHz pmr is given in Table II.

Photolysis of 1-Butyl-1a,9b-9*H*-dihydrophenanthro[9,10-*b*]azirine (**12**) Under Argon.

Typically, a solution of 250 mg of **12** [8] in 200 ml of argon purged dichloromethane was placed in a quartz well and irradiated with a 450 W medium pressure mercury lamp located at a distance of 10 cm from the reaction vessel. The hplc analysis indicated that 90% of the starting material had reacted after 1 hour. The irradiation was discontinued and the solvent evaporated. The residue was extracted several times with boiling cyclohexane and flash chromatographed [13] on silica gel. The first fraction that was eluted with hexane yielded 27 mg of pure phenanthrene (**2**) (17% of unreacted **12**). Addition of 10% ether to the eluent afforded then 90 mg (40%) of *N*-butyl-9-phenanthrenamine (**13**), mp 103-104° (from methanol) (lit [9] mp 102-103°); 300 MHz pmr (deuteriochloroform) 1.019 (t, 3H, J = 7.4 Hz), 1.544 (sextet, 2H, J = 7.4 Hz), 1.789 (quintet, 2H, J = 7.4 Hz), 3.335 (t, 2H, J = 7.4 Hz), 6.762 (s, 1H), 7.36 (td, 1H, J<sub>t</sub> = 8.1 Hz, J<sub>d</sub> = 1.5 Hz), 7.470 (td, 1H, J<sub>t</sub> = 7.4 Hz, J<sub>d</sub> = 1.5 Hz), 7.554-7.662 (m, 2H), 7.687 (d, 1H, J = 8.1 Hz), 7.876 (dd, 1H, J<sub>1</sub> = 8.1 Hz, J<sub>2</sub> = 1.5 Hz), 8.512 (d, 1H, J = 8.1 Hz), 8.680 (dd, 1H, J<sub>1</sub> = 8.1 Hz, J<sub>2</sub> = 1.5 Hz).

Separation of the two photoproducts and the starting material could be accomplished also by an hplc column packed with R.P. 18 and eluted

with 95% aqueous methanol (flow rate 1.6 ml/minute).

Almost the same product distribution and the same yields were obtained when the irradiation was conducted in a Pyrex well. Nor were any changes observed when 0.17 g of sulfur was added to the reaction mixture.

#### Irradiation of **12** in the Presence of Air.

As in the previous experiment, 0.25 g of **12** was irradiated with the aid of a 450 W mercury lamp. However the Argon was substituted by air. After 40 minutes, when hplc analysis indicated that 90% of the starting material had reacted, the solvent was evaporated and the residue extracted several times with boiling cyclohexane. Evaporation of the solvent afforded 180 mg of high boiling material that was flash chromatographed [13] over silica gel. Pure hexane eluted 10 mg of phenanthrene (**2**); hexane-ether (9:1) eluted 44 mg (18%) of *N*-butyl-9-phenanthrenamine (**13**); a mixture of 15% hexane and 85% ether yielded 96 mg (37%) of pale yellow crystals of 2-propylphenanthro[9,10-*d*]oxazole (**14**) as well as 25 mg of unreacted starting material **12**. Compound **14** had mp 85° (from *n*-hexane); ir (Nujol): 1560, 1580 cm<sup>-1</sup> (C=N); uv (dichloromethane): λ max (log ε) 253 (sh) (4.83), 257 (4.89), 277 (4.45), 293 (4.32), 306 nm (4.38); 300 MHz pmr (deuteriochloroform): 1.042 (t, 3H, J = 7.4 Hz), 1.956 (sextet, 2H, J = 7.4 Hz), 3.002 (t, 2H, J = 7.4 Hz), 7.555-7.674 (m, 4H), 8.155 (dd, 1H, J<sub>1</sub> = 7.0 Hz, J<sub>2</sub> = 2.0 Hz), 8.445 (dd, 1H, J<sub>1</sub> = 7.3 Hz, J<sub>2</sub> = 1.7 Hz), 8.640 (dd, 1H, J<sub>1</sub> = 6.3 Hz, J<sub>2</sub> = 1.4 Hz), 8.667 (dd, 1H, J<sub>1</sub> = 7.4 Hz, J<sub>2</sub> = 2.5 Hz); 75 MHz decoupled cmr (deuteriochloroform): 13.826 (CH<sub>3</sub>), 20.929 (CH<sub>2</sub>), 30.862 (CH<sub>2</sub>), 166.192 (OCN), 120.644, 120.770, 121.351, 122.868, 123.500, 123.803, 125.926, 126.154, 126.407, 127.266, 127.443, 128.859, 129.086; ms: (70 eV, 90°) m/e (relative intensity) 261 (M<sup>+</sup>, 100), 246 [(M-CH<sub>3</sub>)<sup>+</sup>, 29], 232 [(M-C<sub>2</sub>H<sub>5</sub>)<sup>+</sup>, 79], 204 (C<sub>15</sub>H<sub>8</sub>O<sup>+</sup>, 15), 164 (C<sub>13</sub>H<sub>8</sub><sup>+</sup>, 25).

Anal. Calcd. for C<sub>18</sub>H<sub>15</sub>NO: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.53; H, 5.97; N, 5.50.

#### Acknowledgement.

We are grateful to the Israel Commission for Basic Research, The Israel Academy of Sciences and Humanities for financial support of this study.

#### REFERENCES AND NOTES

- [1] Part I: M. Weitzberg, Z. Aizenshtat and J. Blum, *J. Heterocyclic Chem.*, **18** 1513 (1981).
- [2] A. brief report on this study was presented at the Eighth International Congress of Heterocyclic Chemistry, Graz, Austria, August, 1981.
- [3a] D. Avnir and J. Blum, *J. Heterocyclic Chem.*, **17**, 1349 (1980);
- [b] K. Ishikawa and G. W. Griffin, *Tetrahedron Letters*, 1369 (1977);
- [c] G. W. Griffin, S. K. Satra and N. E. Brightwell, *ibid.*, 1239 (1976);
- [d] D. M. Jerina, B. Witkop, C. L. McIntosh and O. L. Chapman, *J. Am. Chem. Soc.*, **96**, 5578 (1974); [e] B. L. Van-Duuren, G. Witz and S. L. Agrawal, *J. Org. Chem.*, **39**, 1032 (1974); [f] K. Shudo and T. Okamoto, *Chem. Pharm. Bull.*, **21**, 2809 (1973).
- [4] K. Shudo and T. Okamoto, *ibid.*, **24**, 1013 (1976).
- [5] See e.g., M. Nastasi and J. Streith in "Rearrangements in Ground and Excited States", P. de Mayo, ed, Vol. 3, Academic Press, 1980, Chapter 21.
- [6] J. Schmidt and H. Lumpp, *Ber.*, **43**, 787 (1910).
- [7] R. Japp and A. Findlay, *J. Chem. Soc.*, 1115 (1897).
- [8a] K. H. Grellmann, G. M. Sherman and M. Linschitz, *J. Am. Chem. Soc.*, **85**, 1881 (1963); [b] H. Linschitz and K. H. Grellmann, *ibid.*, **86**, 303 (1964).
- [9] Y. Ittah, I. Shahak and J. Blum, *J. Org. Chem.*, **43**, 392 (1978).
- [10] L. Fieser, R. P. Jacobson and C. C. Price, *J. Am. Chem. Soc.*, **58**, 2163 (1936).
- [11] For an example of hydrogen abstraction α to a nitrogen atom see e.g., T. Matsuura, Y. Ito and I. Saito, *Bull. Chem. Soc. Japan*, **46**, 3805 (1973).
- [12] M. Weitzberg, Z. Aizenshtat, P. Jerushalmy and J. Blum, *J. Org. Chem.*, **45**, 4252 (1980).
- [13] W. C. Still, M. Kahn and A. Mitra, *ibid.*, **43**, 2923 (1978).
- [14] B. Schiedt, *J. Prakt. Chem., N. F.*, **157**, 203 (1941).
- [15] We believe that the mp given by Schmidt and Lumpp [6] is incorrect since we failed in all of our attempts to prepare **5** according to their procedure. We were also unsuccessful in trials to raise the mp by further chromatography and successive recrystallizations.