

Studies on the Syntheses of Azole Derivatives. Part VIII (1).  
 Photolysis of *N*-Aryl-*N*-benzylcarbamoyl Azides  
 [Studies on the Syntheses of Heterocyclic Compounds. Part CDXV (2)]

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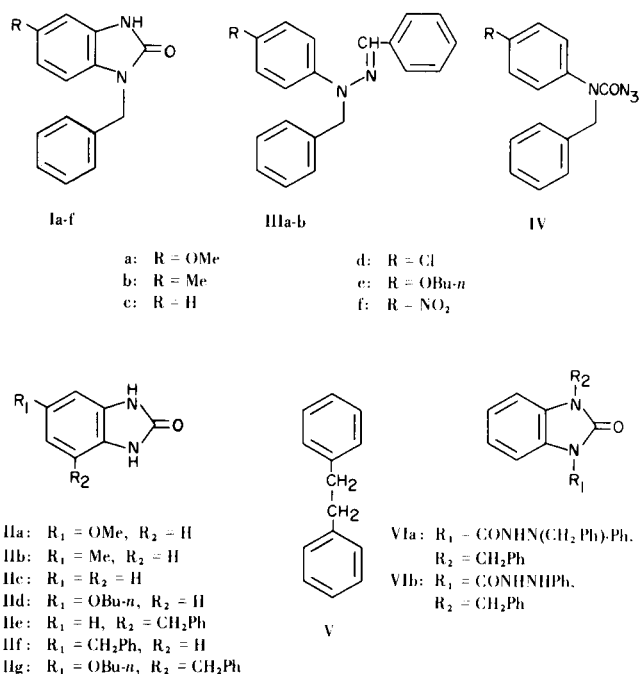
Photolysis of *N*-benzyl-*N*-phenylcarbamoylazide (IVc) afforded 1-benzyl-2-benzimidazolinone (Ic), 2-benzimidazolinone (IIc), 4-benzyl-2-benzimidazolinone (IIe), and 5-benzyl-2-benzimidazolinone (IIf). The same reaction of *N*-benzyl-*N*-(4-chlorophenyl)carbamoyl azide (IVd) gave 3-benzyl-1-(phenylhydrazocarbonyl)-2-benzimidazolinone (VIb) besides the above four products. In the case of *N*-benzyl-4-(4-butoxyphenyl)carbamoyl azide (IVe), 1-benzyl-5-butoxy-2-benzimidazolinone (Ie), 5-butoxy-2-benzimidazolinone (IIId), 5-benzyl-2-benzimidazolinone (IIIf), and 4-benzyl-6-butoxy-2-benzimidazolinone (IIIfg).

In the previous paper (4) the syntheses of 2-benzimidazolinones (Ia,b and IIa,b) and *N*-benzyl-*N*<sup>1</sup>-benzylidene-*N*-(4-substituted phenyl)hydrazines (IIIa and IIIb) through the photolysis of *N*-benzyl-*N*-(4-methoxyphenyl)carbamoyl azide (IVa) and *N*-benzyl-*N*-(4-methylphenyl)carbamoyl azide (IVb) were reported. We have recently investigated the photolysis of several *N*-benzyl-*N*-phenylcarbamoyl azides (IVc-f) and herein report these results.

First, *N*-benzyl-*N*-phenylcarbamoyl azide (IVc) (5) was irradiated using a Hanovia 450 W mercury lamp in the presence of a vycor filter under cooling for 20 hours. After irradiation, the reaction product, obtained by the usual work-up, was chromatographed on silica gel.

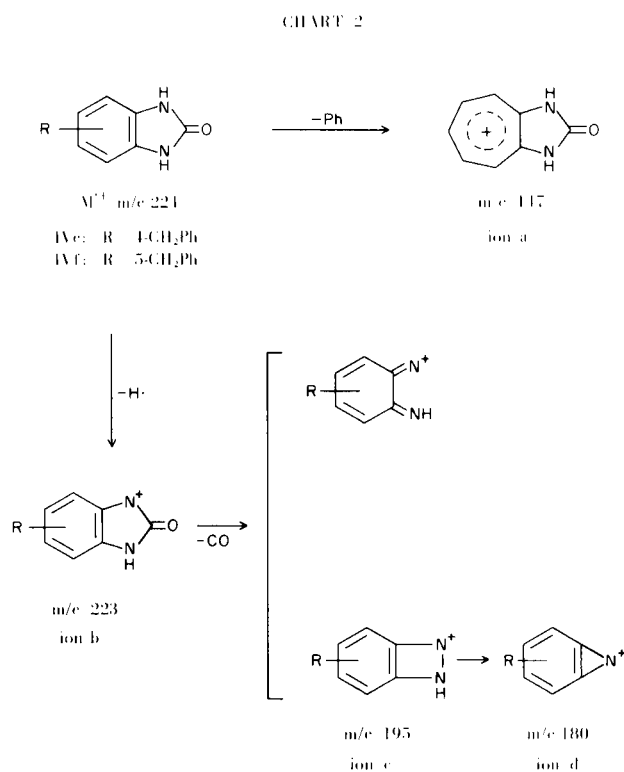
Evaporation of the benzene eluate gave 1,2-diphenyl-ethane (V) (6) in 6.7% yield, and removal of the subsequent chloroform eluate afforded 1-benzyl-2-benzimidazolinone (Ic) (5) in 10.9% yield. These products (V and Ic) were identified by a mixed melting point test and comparison of the spectroscopic data. Evaporation of the eluate with chloroform-ethyl acetate (9:1) left 4-benzyl-2-benzimidazolinone (IIe), which was identified by microanalysis and spectra. Its nmr spectrum showed two singlets at 10.53 and 10.75 ppm attributable to NH protons, aromatic protons due to phenyl group (5H) as singlet at 7.21, and the methylene protons (2H) due to diphenyl methane as singlet at 3.95. The other aromatic protons were observed at 6.76 ppm as singlet. The ir spectrum showed absorption due to ureide NH and a carbonyl group at 3320-2700 and

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1715 cm<sup>-1</sup>, respectively. The uv spectrum, which supported the presence of a 2-benzimidazolinone skeleton, was similar to that of Ic, IIb, and IIc (Fig. 1). The mass spectrum gave the main fragments at m/e 224 (M<sup>+</sup>), 223

( $M^+ - 1$ ), 195, 180, 147, 91, and 77, and the fragmentation pattern (*cf.* Chart 2) (8) was extremely similar to that of 5-benzyl-2-benzimidazolinone (II<sub>f</sub>) synthesized as described later. Accordingly, this product was assigned the structure (II<sub>e</sub>).



Evaporation of the following eluate using chloroform-ethyl acetate (9:1) as solvent afforded 5-benzyl-2-benzimidazolinone (II<sub>f</sub>). Spectroscopic data were identical with those of the authentic specimen, prepared by the reduction of 3,4-dinitrobenzophenone (VII), followed by the cyclization of 2-amino-4-benzylaniline (VIII) with urea. Furthermore, its uv (Fig. 1), ir, mass ( $M^+$ ,  $m/e$  244), and nmr spectra confirmed this structure.

The second eluate with chloroform-ethyl acetate (1:1) on evaporation afforded 2-benzimidazolinone (II<sub>c</sub>) (7) which was identical with the authentic specimen.

Secondly, *N*-benzyl-*N*-(4-chlorophenyl)carbamoyl azide (IV<sub>d</sub>) was irradiated and, after the work-up similar to the case of IV<sub>c</sub>, the reaction products afforded 1-benzyl- (I<sub>c</sub>) (5), 4-benzyl- (II<sub>e</sub>) and 5-benzyl-2-benzimidazolinone (II<sub>f</sub>), 2-benzimidazolinone (II<sub>c</sub>), and 3-benzyl-1-(phenylhydrazocarbonyl)-2-benzimidazolinone (VI<sub>b</sub>). In this case, the formation of 1,2-diphenylethane (V) was not observed. The structure of VI<sub>b</sub> was assigned on the basis of microanalysis and spectroscopic data. Its ir spectrum (potassium bromide) showed the absorption bands due to NH at 3350 and 3215  $\text{cm}^{-1}$  and C=O bands at 1732 and

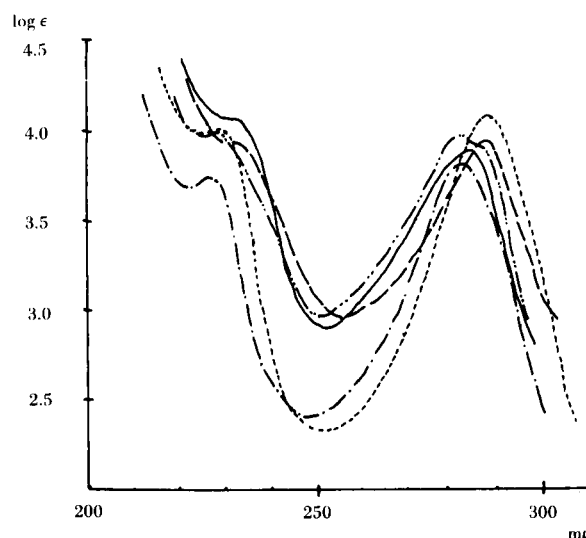


Figure I. UV (EtOH)

5-methyl-2-benzimidazolinone (II <sub>b</sub> )	-----
2-benzimidazolinone (II <sub>c</sub> )	- - - - -
1-benzyl-2-benzimidazolinone (I <sub>c</sub> )	- · - · - ·
4-benzyl-2-benzimidazolinone (II <sub>e</sub> )	—————
5-benzyl-2-benzimidazolinone (II <sub>f</sub> )	- - - - -

1712  $\text{cm}^{-1}$ . Its nmr spectrum showed a quartet ( $J = 6.0$  and 3.0 Hz) at 8.24 ppm due to C<sub>7</sub>-H; and the other aromatic protons were observed at 6.20-7.40 ppm (8H) and 7.30 ppm (5H) as multiplet and singlet, respectively.

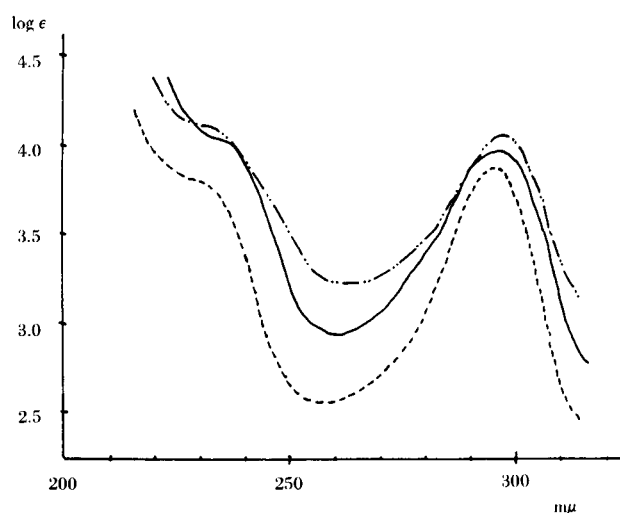


Figure II. UV (EtOH)

1-benzyl-5-butoxy-2-benzimidazolinone (I <sub>e</sub> )	-----
5-butoxy-2-benzimidazolinone (II <sub>d</sub> )	- - - - -
4-benzyl-6-butoxy-2-benzimidazolinone (II <sub>g</sub> )	—————

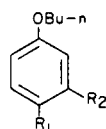
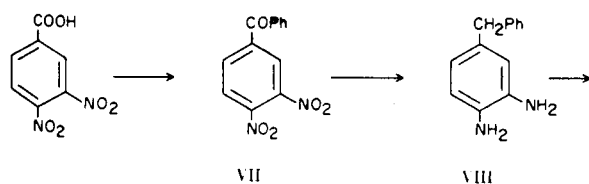
The methylene proton on the benzyl group was observed at 5.06 ppm as singlet. These spectral data were similar to those of VIa. The treatment of VIb with sodium ethoxide in ethanol gave 1-benzyl-2-benzimidazolinone (Ic). This fact indicated that the benzyl group was located at the N<sub>1</sub>-position.

The irradiation of *N*-benzyl-*N*-(4-butoxyphenyl)carbamoyl azide (IVe) gave 1,2-diphenylethane (V), 1-benzyl-5-butoxy-2-benzimidazolinone (Ie) (5), 4-benzyl-6-butoxy-2-benzimidazolinone (IIg), 5-benzyl-2-benzimidazolinone (IIf) and the 5-butoxy-derivative (II d). The structural proof of IIg was verified by microanalysis and spectroscopic data. Its uv spectrum (Fig. II) indicated the presence of a 2-benzimidazolinone skeleton and its nmr spectrum supported the presence of a butoxy group and two NH protons. The phenyl and methylene signals due to the benzyl group were observed at 7.20 (5H) and 3.98 ppm (2H) as singlets. The other two aromatic protons (2H) were observed at 6.46 and 6.53 ppm as two doublets ( $J = 2.5$  Hz). This fact indicates that the butoxy group is located at the C-6 position and the position of the benzyl group should be *meta* to the butoxy group. The 5-butoxy derivative (II d) was identical with the authentic sample synthesized by the cyclization of 1,2-diamino-4-butoxybenzene (XI) with urea. Irradiation of the carbamoyl azides (IVc,d,e) afforded the products described above as well as other polymerized products.

Finally, the irradiation of *N*-benzyl-*N*-(4-nitrophenyl)carbamoyl azide (IVf) was examined under similar conditions. However, no formation of 2-benzimidazolinone derivatives was observed.

Thus, carbamoyl azide (Vc,d,e) was found to hinder the Curtius rearrangement occurring on thermal reaction of the azide (5). Furthermore, the cleavage of the *N*-benzyl group and the reaction of a free benzyl radical were found to occur during the above reaction.

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- IX:  $R_1 = NHAc$ ,  $R_2 = NO_2$   
 X:  $R_1 = NH_2$ ,  $R_2 = NO_2$   
 XI:  $R_1 = R_2 = NH_2$

## EXPERIMENTAL (9)

Photolysis of *N*-Benzyl-*N*-phenylcarbamoyl Azide (IVc).

A solution of 2.8 g. of carbamoyl azide (IVc) (2) in 700 ml. of tetrahydrofuran was irradiated under a current of nitrogen using a 450 W Hanovia high pressure mercury arc lamp (679 A-36) and vycor filter for 20 hours with water-cooling. Evaporation of the solvent *in vacuo* gave a syrup to which was added 40 ml. of benzene and kept aside at room temperature to give 334 mg. of crystals (A), which were then filtered. Evaporation of the benzene filtrate gave a syrup, which was chromatographed on 130 g. of silica gel (Wakogel, 100-200 mesh). The first benzene eluate (F<sub>1-8</sub>, each 120 ml.) gave 820 mg. of a brown powder. The second benzene eluate (F<sub>9-10</sub>, each 100 ml.) afforded 72 mg. (6.7%) of a solid which was crystallized from aqueous ethanol to give 1,2-diphenylethane as colorless scales, m.p. 52-53°, identical with an authentic sample [lit. (6), m.p. 53°] by mixed melting point and comparison of spectroscopic data. After the removal of a tar (220 mg.) from the eluate with benzene-chloroform (1:1) (F<sub>11-18</sub>, each 300 ml.), benzene-chloroform (1:1) (F<sub>19-31</sub>, each 300 ml.) and chloroform-ethyl acetate (9:1) (F<sub>32</sub>, 300 ml.) eluates were evaporated to afford 280 mg. (10.96%) of pale brown crystals, which were recrystallized from ethyl acetate to give 1-benzyl-2-benzimidazolinone (Ic) as colorless needles, m.p. 197-198°, identical with an authentic sample [lit. (5), m.p. 197-198°];  $\lambda$  max (ethanol)  $m\mu$  (log  $\epsilon$ ) 228.2 (2.98) (shoulder), 282.0 (3.96). The successive eluate with chloroform-ethyl acetate (9:1) (F<sub>33-35</sub>, was washed with 1 ml. of ether-ethyl acetate (1:1) to give 102 mg. (3.9%) of 4-benzyl-2-benzimidazolinone (IIe) as colorless needles, m.p. 206-207° (from ethyl acetate);  $\nu$  max (potassium bromide)  $cm^{-1}$ : 3320-2700 (NH), 1715 (C=O), 1665 (associated C=O),  $\nu$  max (CHCl<sub>3</sub>)  $cm^{-1}$ : 3480, 3300-2700 (NH), 1710 (C=O);  $\lambda$  max (ethanol)  $m\mu$  (log  $\epsilon$ ) 233 (4.06) (shoulder), 284.5 (3.80); nmr  $\delta$  (deuteriodimethylsulfoxide): 10.75, 10.53 (each 1H, broad singlet, each NH), 7.21 (5H, singlet, C<sub>6</sub>H<sub>5</sub>), 6.76 (3H, singlet, C<sub>4</sub>-H, C<sub>5</sub>-H, C<sub>6</sub>-H), 3.95 (2H, singlet, -CH<sub>2</sub>-); mass spectrum  $m/e$ : 224 (M<sup>+</sup>) (100%), 223 (25), 195 (18), 180 (11), 147 (28), 146 (15), 91 (8), 77 (6).

*Anal.* Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O: C, 74.99; H, 5.38; N, 12.49. Found: C, 75.24; H, 5.53; N, 12.39.

The fraction (F<sub>36-39</sub>, each 300 ml.) with chloroform-ethyl acetate (9:1) gave 265 mg. (10.1%) of colorless crystals, which were recrystallized from ethyl acetate to give 5-benzyl-2-benzimidazolinone (II f) as colorless needles, m.p. 254-255°, identical with an authentic sample synthesized by another method described later;  $\nu$  max (potassium bromide)  $cm^{-1}$ : 3250-2650 (NH), 1730 (C=O);  $\lambda$  max (ethanol)  $m\mu$  (log  $\epsilon$ ): 232.8 (3.92) (shoulder), 287.5 (3.94); nmr  $\delta$  (deuteriodimethylsulfoxide): 10.45 (2H, broad signal, 2 x NH), 7.19 (5H, singlet, C<sub>6</sub>H<sub>5</sub>), 6.78 (2H, singlet, C<sub>6</sub>-H, C<sub>7</sub>-H), 6.72 (1H, singlet, C<sub>5</sub>-H), 3.88 (2H, singlet, -CH<sub>2</sub>-); mass spectrum  $m/e$ : 224 (M<sup>+</sup>) (100%), 223 (34), 195 (7), 180 (11), 147 (41), 146 (6), 91 (7), 77 (6).

*Anal.* Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O: C, 74.99; H, 5.38; N, 12.49. Found: C, 75.14; H, 5.42; N, 12.48.

Finally, chloroform-ethyl acetate (1:1) eluate (F<sub>40-43</sub>, each 300 ml.) gave colorless crystals (269 mg.) to which was added crystals (A) (334 mg.) obtained before [total yield is 38.2%]. Recrystallization from ethanol gave 2-benzimidazolinone (IIc) as colorless needles, m.p. 305-306°, which were identical with the authentic sample [lit. (7), m.p. 310°];  $\lambda$  max (ethanol)  $m\mu$  (log  $\epsilon$ ) 226.6 (3.76) (shoulder), 281.7 (3.80).

Photolysis of *N*-Benzyl-*N*-(4-chlorophenyl)carbamoyl Azide (IVd).

A solution of 2.9 g. of IVd in 700 ml. of tetrahydrofuran was

irradiated for 20 hours in the same way as IVc. The solvent was evaporated, and the mixture was then separated by silica gel column chromatography using 150 g. of silica gel, the first benzene eluate (F<sub>1-20</sub>, each 50 ml.) and benzene-chloroform eluate (F<sub>21-42</sub>, each 50 ml.) gave 500 mg. of a dark brown powder. After the removal of a tar (800 mg.) from chloroform eluate (F<sub>43-49</sub>, each 200 ml.), the second chloroform eluate (F<sub>50-55</sub>, each 200 ml.) gave 98 mg. (5.4%) of colorless crystals which were recrystallized from benzene-*n*-hexane (1:1) to give 3-benzyl-1-(phenylhydrazocarbonyl)-2-benzimidazolinone (VIb) as colorless needles, m.p. 165-166° (Beilstein test is negative);  $\nu$  max (potassium bromide)  $\text{cm}^{-1}$ : 3350, 3215 (NH), 1732, 1712 (C=O); nmr  $\delta$  (deuteriochloroform): 8.65, 5.60 (each 1H, broad signal, each NH), 8.24 (1H, quartet,  $J = 6.0, 3.0$  Hz, C<sub>7</sub>-H), 6.20-7.40 (8H, multiplet, C<sub>4</sub>-H, C<sub>5</sub>-H, C<sub>6</sub>-H, N-C<sub>6</sub>H<sub>5</sub>), 7.30 (5H, singlet, C-C<sub>6</sub>H<sub>5</sub>), 6.05 (2H, singlet, -CH<sub>2</sub>-).

*Anal.* Calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>: C, 70.37; H, 5.06; N, 15.63. Found: C, 70.47; H, 4.96; N, 15.61.

The chloroform-ethyl acetate (9:1) eluate (F<sub>56-58</sub>, each 200 ml.) afforded 325 mg. (14.3%) of colorless crystals which gave a negative Beilstein test and recrystallized from ethyl acetate to give 1-benzyl-2-benzimidazolinone (Ic) as colorless needles, m.p. 197-198°, identical with an authentic sample (5). Successively 152 mg. of an oily substance obtained from chloroform-ethyl acetate (9:1) (F<sub>59-61</sub>, each 250 ml.), (4:1) (F<sub>62-66</sub>, each 250 ml.), and chloroform-ethyl acetate (1:1) (F<sub>67-68</sub>, each 250 ml.) eluates, was washed with 1 ml. of ether-ethyl acetate (1:1) to give 100 mg. (4.4%) of crystals which showed negative on the Beilstein test and recrystallized from ethyl acetate to give 4-benzyl-2-benzimidazolinone (IIe) as colorless needles, m.p. 206-207°, identical with IIe obtained by the photolysis of IVc on the mixed melting point test. The chloroform-ethyl acetate (1:1) (F<sub>69-74</sub>, each 250 ml.) gave 160 mg. (7.0%) of 5-benzyl-2-benzimidazolinone (IIf) which was recrystallized from ethyl acetate to give colorless needles, m.p. 254-255°. The spectroscopic data agreed with those of IIf obtained by photolysis of IVc. Finally, chloroform-ethyl acetate (1:1) eluate (F<sub>75-79</sub>, each 250 ml.) gave 180 mg. (13.3%) of 2-benzimidazolinone (IIc), which showed negative on the Beilstein test and recrystallized from ethanol to give colorless needles, m.p. 205-206°, identical with the authentic sample (7).

Photolysis of *N*-Benzyl-*N*-(4-butoxyphenyl)carbamoyl Azide (IVe).

A solution of 3 g. of IVe in 700 ml. of tetrahydrofuran was irradiated for 20 hours under the same conditions as above. Evaporation of the solvent was followed by silica gel column chromatography using 150 g. of silica gel. The first benzene eluate (F<sub>1-5</sub>, each 200 ml.) and benzene-chloroform (1:1) eluate (F<sub>6-9</sub>, each 200 ml.) were evaporated to give a brownish powder (520 mg.), which was extracted with hot *n*-hexane. Removal of the extract afforded 70 mg. (8.0%) of 1,2-diphenylethane, m.p. 52-53° (from aqueous ethanol), which was identical with the authentic sample [lit. (6), m.p. 53°]. The chloroform eluate (F<sub>10-12</sub>, each 300 ml.) and chloroform-ethyl acetate (4:1) eluate (F<sub>13-21</sub>, each 100 ml.) gave 469 mg. of a tar and the second chloroform-ethyl acetate (4:1) eluate (F<sub>22-24</sub>, each 300 ml.) afforded 33 mg. (1.2%) of crystals which were recrystallized from ethyl acetate to give 1-benzyl-5-butoxy-2-benzimidazolinone (Ie) as colorless needles, m.p. 142-143°, identical with an authentic sample [lit. (5), m.p. 142-143°];  $\lambda$  max (ethanol)  $\mu\text{m}$  ( $\log \epsilon$ ) 232.6 (4.10) (shoulder), 297.0 (4.06). Successively, chloroform-ethyl acetate (4:1) eluate (F<sub>25-31</sub>, each 300 ml.) gave 120 mg. of a syrup, which was washed with 1.5 ml. of ethyl acetate-ether (1:2) to give 75 mg. (2.6%) of dried crystals. Recrystallization

from ethyl acetate gave 4-benzyl-6-butoxy-2-benzimidazolinone (IIg) as colorless needles, m.p. 194-195°;  $\nu$  max (potassium bromide)  $\text{cm}^{-1}$ : 3200-2700 (NH), 1695 (C=O),  $\lambda$  max (ethanol)  $\mu\text{m}$  ( $\log \epsilon$ ) 235.0 (4.03) (shoulder), 296.0 (3.98); nmr  $\delta$  (deuteriochloroform) ppm: 10.05, 9.35 (each 1H, broad signals, each NH), 7.20 (5H, singlet, C<sub>6</sub>H<sub>5</sub>), 2.98 (2H, singlet, -CH<sub>2</sub>Ph), 6.53 (1H, doublet,  $J = 2.5$  Hz, C<sub>4</sub>-H or C<sub>6</sub>-H), 6.46 (1H, doublet,  $J = 2.5$  Hz, C<sub>6</sub>-H or C<sub>4</sub>-H), 3.84 (2H, triplet,  $J = 6.0$  Hz, OCH<sub>2</sub>CH<sub>2</sub>), 1.15-1.85 (4H, multiplet, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.95 (3H, triplet, -CH<sub>2</sub>CH<sub>3</sub>); mass spectrum  $m/e$ : 296 ( $M^+$ ).

*Anal.* Calcd. for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.99; H, 6.61; N, 9.24.

The fourth chloroform-ethyl acetate (4:1) eluate (F<sub>32</sub>, 300 ml.) and (3:2) eluate (F<sub>33-35</sub>, each 300 ml.) afforded 114 mg. (5.3%) of crystals which were recrystallized from ethyl acetate to give 5-benzyl-2-benzimidazolinone (IIf) as colorless needles, m.p. 254-255°, identical with IIf obtained by photolysis IVc and IVd by the mixed melting point test and spectroscopic comparison. Finally, chloroform-ethyl acetate (3:2) eluate (F<sub>36-46</sub>, each 300 ml.) and (1:1) eluate (F<sub>47-51</sub>, each 300 ml.) gave 537 mg. (27.0%) of crystals which were recrystallized from ethyl acetate to give 5-butoxy-2-benzimidazolinone (IId) as colorless needles, m.p. 252-253°, identical with an authentic sample prepared by another method described later;  $\nu$  max (potassium bromide)  $\text{cm}^{-1}$ : 3200-2700 (NH), 1755 (C=O);  $\lambda$  max (ethanol)  $\mu\text{m}$  ( $\log \epsilon$ ) 230.0 (3.82) (shoulder), 295.0 (3.89); nmr  $\delta$  (deuterio-dimethylsulfoxide) ppm: 10.42, 10.28 (each 1H, broad singlets, each NH), 6.78 (1H, doublet,  $J = 9.0$  Hz, C<sub>7</sub>-H), 6.49 (1H, doublet,  $J = 3.0$  Hz, C<sub>4</sub>-H), 6.48 (1H, quartet,  $J = 9.0, 3.0$  Hz, C<sub>6</sub>-H), 3.86 (2H, triplet,  $J = 6.0$  Hz, OCH<sub>2</sub>CH), 1.10-1.85 (4H, multiplet, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.90 (3H, triplet,  $J = 6.0$  Hz, CH<sub>2</sub>CH<sub>3</sub>); mass spectrum  $m/e$ : 206 ( $M^+$ ).

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.35; H, 6.85; N, 13.81.

### 3,4-Dinitrobenzophenone (VII).

To a suspension of 5 g. (0.023 mole) of 3,4-dinitrobenzoic acid in 100 ml. of dry benzene was added 6.8 g. (0.033 mole) of phosphorus pentachloride. This was stirred for 30 minutes at 60° (bath temperature). After cooling, 9.2 g. (0.069 mole) of aluminum chloride was added under cooling on an ice water-bath, and, after 10 minutes, the mixture was stirred for an additional 45 minutes at 90° (bath). The reaction mixture was decomposed with 100 g. of ice water and 10 ml. of concentrated hydrochloric acid as usual. Evaporation of the organic layer gave an oily product which was recrystallized from isopropyl ether to give VII (4.5 g., 70.3%) as pale orange needles, m.p. 82-83°;  $\nu$  max (potassium bromide)  $\text{cm}^{-1}$ : 1670 (C=O).

*Anal.* Calcd. for C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>O<sub>5</sub>: C, 57.36; H, 2.96; N, 10.29. Found: C, 57.51; H, 2.78; N, 10.09.

### 1,2-Diamino-4-benzylbenzene (VIII).

To zinc amalgam [prepared from 15 g. (0.23 mole) of zinc, 1.5 g. of mercuric chloride, 22.5 ml. of water and 1 ml. of concentrated hydrochloric acid] was added by the usual method a mixture of 4 ml. of water, 9 ml. of concentrated hydrochloric acid, 5 ml. of toluene and 1 g. (0.0037 mole) of 3,4-dinitrobenzophenone (VII). The resulting mixture was then heated for 6 hours on wire netting with stirring. During the above reaction, 4 ml. of concentrated hydrochloric acid was added. After cooling, an aqueous layer was separated. To this was added an excess of 10% sodium hydroxide. The alkaline mixture was extracted with benzene; then the extract was washed with water, dried over

sodium sulfate, and evaporated to give a syrup, which was chromatographed on silica gel with chloroform-ethanol (10:1) to give 0.46 g. (46.5%) of VIII;  $\nu$  max (potassium bromide)  $\text{cm}^{-1}$ : 3460, 3380, 3250 ( $\text{NH}_2$ ); nmr  $\delta$  (deuteriochloroform): 3.20 (4H, broad signal, 2 x  $\text{NH}_2$ ), 3.80 (2H, singlet,  $-\text{CH}_2-$ ), 6.46 (1H, singlet,  $\text{C}_3\text{-H}$ ), 6.54 (2H, singlet,  $\text{C}_5\text{-H}$ ), 7.20 (5H, singlet,  $\text{C}_6\text{H}_5$ ). The hydrochloride prepared as usual was recrystallized from ethanol-isopropyl ether to give colorless needles, m.p. 191-192° dec.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$ : C, 57.58; H, 5.95; N, 10.33. Found: C, 57.87; H, 5.88; N, 10.70.

#### 5-Benzyl-2-benzimidazolinone (IIf).

A mixture of 0.27 g. (0.001 mole) of dihydrochloride of VIII and 0.09 g. (0.0015 mole) of urea was heated for 15 minutes at 150-160°. The reaction mixture was recrystallized from ethanol to give 140 mg. (63.6%) of IIf as colorless needles, m.p. 254-255°.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$ : C, 74.99; H, 5.38; N, 12.49. Found: C, 74.72; H, 5.55; N, 12.60.

#### The Thermal Decomposition of VIb in the Presence of Sodium Ethoxide.

A solution of 90 mg. of IVb in ethanolic sodium ethoxide solution [prepared from 60 ml. of ethanol and 0.5 g. of metallic sodium] was heated at 200° for 5 hours in a sealed tube. After the reaction, the solvent was evaporated to give a residue, the aqueous solution of which was washed with ether, acidified with hydrochloric acid and extracted with ethyl acetate. Evaporation of the extract gave 51 mg. (90.0%) of 1-benzyl-2-benzimidazolinone (Ic) as colorless needles, m.p. 197-198°, identical with the authentic sample (5).

#### 4-Butoxy-2-nitroacetanilide (IX).

To a mixture of 90 ml. of glacial acetic acid, 65 ml. of water was added 48.5 g. of *p*-butoxyaniline under stirring at room temperature. When the *p*-butoxyaniline had dissolved, 100 g. of ice was added when the temperature reached 0-5°, 31 ml. of acetic anhydride was added at once under vigorous stirring. The reaction mixture was heated on a water-bath until the crystalline material dissolved and then was cooled with stirring to 45°. To the resulting cooled mixture was added at once 35 ml. of concentrated nitric acid (sp. gr. 1.38), the temperature rising rapidly to 75° and soon beginning to fall. By suitable adjustment of the ice-bath, the temperature was maintained at 60-65° for 10 minutes and then kept at 25° for 10 minutes. The solution was chilled overnight in an ice-box and the precipitate was collected, washed with 80 ml. of ice-water and dried to give 63.9 g. (86.3%) of yellow crystals which were recrystallized from aqueous ethanol to give yellow needles, m.p. 85-86°;  $\nu$  max (potassium bromide)  $\text{cm}^{-1}$ : 1518, 1340 ( $\text{NO}_2$ ), 1678 ( $\text{C}=\text{O}$ ), 3340 ( $\text{NH}$ ); nmr  $\delta$  (deuteriochloroform): 7.50 (1H, doublet,  $J = 2.5$  Hz,  $\text{C}_3\text{-H}$ ), 7.30, quartet,  $J = 9.0, 2.5$  Hz,  $\text{C}_5\text{-H}$ ), 7.56 (1H, doublet,  $J = 9.0$  Hz,  $\text{C}_6\text{-H}$ ), 2.05 (3H, singlet,  $-\text{COCH}_3$ ), 4.07 (2H, triplet,  $J = 6.0$  Hz,  $\text{OCH}_2\text{CH}_2$ ), 1.18-1.84 (4H, multiplet,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.96 (3H, triplet,  $J = 6.0$  Hz,  $\text{CH}_2\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_4$ : C, 57.13; H, 6.39; N, 11.11. Found: C, 57.30; H, 6.36; N, 11.23.

#### 4-Butoxy-2-nitroaniline (X).

A mixture of 28 g. (0.5 mole) of potassium hydroxide, 20 ml. of water, 50 ml. of methanol and 63 g. (0.25 mole) of IX was refluxed for 20 minutes on a water-bath. After the addition of

79 ml. of hot water, the mixture was stirred on a water-bath for an additional 15 minutes and then was cooled with ice to give 50.8 g. (96.8%) of crystals. These were recrystallized from aqueous ethanol to give X as reddish orange needles, m.p. 64-65°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_3$ : C, 57.13; H, 6.71; N, 13.33. Found: C, 57.40; H, 6.65; N, 13.42.

#### 1,2-Diamino-4-butoxybenzene (XI).

After 6.3 g. of X was added in three portions to a solution of 27 g. of stannous chloride dihydrate in 36 ml. of concentrated hydrochloric acid with stirring at 85°, the mixture was stirred at 100° for 20 minutes, and was then cooled to give crystals which were made basic with an excess of 10% sodium hydroxide and extracted with benzene. The benzene extract was washed with water, dried over sodium sulfate and evaporated to give 3.3 g. of crude crystals. The hydrochloride prepared as usual was recrystallized from ethanol to give XI hydrochloride as pale reddish brown needles, m.p. 152-153° dec.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O} \cdot 2\text{HCl}$ : C, 47.44; H, 7.17; N, 11.07. Found: C, 47.79; H, 7.00; N, 11.01.

#### 5-Butoxy-2-benzimidazolinone (IIId).

A mixture of 0.6 g. (0.0024 mole) of dihydrochloride of XI and 0.3 g. (0.0048 mole) of urea was heated for 15 minutes at 160-170°. Then the reaction mixture was recrystallized from ethanol to give 0.38 g. (66.7%) of IIId as colorless needles, m.p. 252-253°.

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2$ : C, 64.06; H, 6.84; N, 13.58. Found: C, 64.29; H, 6.88; N, 13.69.

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