

The Photocyclization of 1-( $\alpha$ -Indolyl)-2-( $\beta$ -pyridyl)acrylonitrile

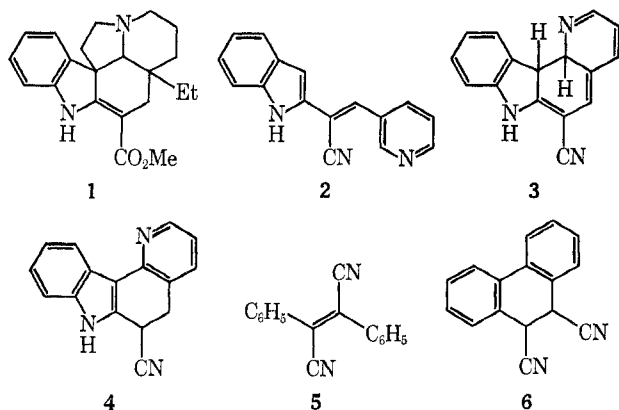
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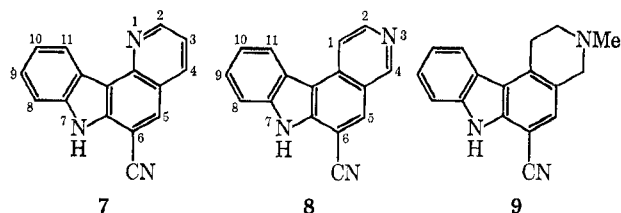
The photolysis of an ethanol solution of the title compound in the presence of ferric chloride or iodine has yielded 6-cyano-7H-pyrido[3,2-c]carbazole and 6-cyano-7H-pyrido[3,4-c]carbazole. A similar photolysis in the absence of oxidizing agents has led to 1-cyano-3-( $\beta$ -formylvinyl)carbazole.

One of the many conceivable routes of synthesis of *Aspidosperma* alkaloids, e.g., vincadifformine (1), involves the construction of a tetracyclic nucleus, such as 4, and later introductions of the angular two-carbon substituent and the  $\beta$ -indolyl-N<sub>6</sub> ethano bridge. In pursuit of this goal, the synthesis of nitrile 4 was attempted. It was assumed that the photolysis of 1-( $\alpha$ -indolyl)-2-( $\beta$ -pyridyl)acrylonitrile (2) would yield 4 in analogy to the photochemical conversion of the dicyanostilbene 5 into the dihydrophenanthrene 6.<sup>1-3</sup> While this proved not to be the case, an interesting new rearrangement was encountered.

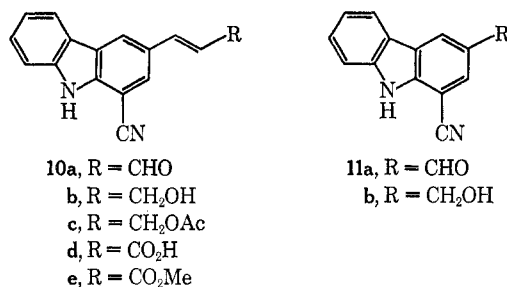


Methoxide-induced condensation of  $\alpha$ -indolylacetonitrile<sup>4</sup> with nicotinaldehyde yielded a single product 2 (or its geometric isomer).<sup>5</sup> Determination of its stereochemistry could be avoided, since its subsequent photocyclization was expected to be preceded by photoisomerization of its central double bond. The photolysis of 2 was first executed in an oxidative manner, in order to ascertain the ease and direction of cyclization and to avoid possible complications during the desired isomerization of the anticipated, sensitive intermediate 3 into 4. Irradiation of an ethanolic solution of 2 with a high-pressure Hanau lamp in the presence of ferric chloride or iodine led to two products, 7 and 8, in 5 and 30% yields, respectively. The spectral characteristics of the

pyridocarbazoles were in consonance with their assigned structures, the most striking features being the deshielding of the C-11 proton by the nonbonded electron pair of N-1 in the proton magnetic resonance spectrum of the less polar substance 7 and the deshielding of the C-4 proton by the central benzene ring in the spectrum of 8 (see Experimental Section). The heterocycle 7, containing a highly hindered pyridine nitrogen, was unreactive toward methylation, whereas 8 yielded a pyridinium salt on treatment with methyl iodide, which could be converted into the piperidine derivative 9 on sodium borohydride reduction. The mass spectrum of the latter product revealed an  $M - 43$  peak, characteristic of the  $\text{CH}_2=\text{NCH}_3$  moiety and indicative of the lack of attachment of the piperidine nitrogen to the carbazole nucleus.



Irradiation of an ethanolic solution of 2 under nitrogen with a high-pressure Hanau lamp yielded a complex mixture from which a product to which structure 10a was assigned could be isolated in 30% yield. Its reduction with sodium borohydride gave the alcohol 10b whose acetylation afforded the ester 10c, while its oxidation with osmium tetroxide and thereafter with sodium periodate yielded 1-cyano-3-formylcarbazole (11a). Borohydride reduction of the latter led to the alcohol 11b, whereas condensation with malonic acid gave the cinnamic acid derivative 10d, the reduction of whose acid chloride with lithium tri-*t*-butoxyaluminum hydride produced an alcohol identical with the product (10b) of reduction of the photolysis product. The last set of experiments verified the *trans* configuration of the side chain of 10a, already discernible from its pmr spectrum.



The formation of 10a from the photolysis of 2 implicates 3 and 12 as consecutive intermediates. While

(1) M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, **85**, 2186 (1963); *J. Chem. Soc.*, 5544 (1964).

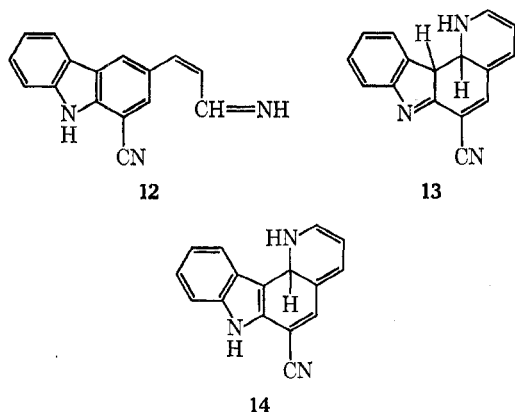
(2) For reviews of the photochemical transformation of stilbenes into dihydrophenanthrenes or phenanthrenes, see (a) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 219-222; (b) F. R. Stermitz in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 247; (c) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, Chapters 13 and 14, pp 126-145; (d) K. A. Muskat and E. Fischer, *J. Chem. Soc., B*, 662 (1967).

(3) For examples of the conversion of stilbazoles into azodihydrophenanthrenes or azophenanthrenes, see ref 2a-c and (a) C. E. Loader and C. J. Timmons, *J. Chem. Soc., C*, 1078 (1966); 1457 (1967); 330 (1968); (b) V. M. Clark and A. Cox, *Tetrahedron*, **22**, 3421 (1966); (c) E. Winterfeldt and H. J. Altmann, *Angew. Chem.*, 486 (1968).

(4) W. Schindler, *Helv. Chim. Acta*, **40**, 2156 (1957).

(5) This compound was synthesized initially by Dr. T. Oishi (E. Wenkert and T. Oishi, unpublished observations).

the unravelling of the pyridine ring is unprecedented,<sup>6</sup> it represents an elimination-aromatization reminiscent of the spontaneous formation of phenanthrenes from dihydrophenanthrene intermediates possessing leaving groups at central bridgehead positions in the photocyclization of *o*-halo- or *o*-methoxystilbenes.<sup>7</sup> Alternatively, **3** in ethanol solution can be expected to be in equilibrium with its tautomers **13** and **14**, of which the latter can undergo an electrocyclic transformation into **12**. The available experimental facts were insufficient to differentiate these reaction routes or to discern the sequence of events in the hydrolytic isomerization of **12** into **10a** (photolysis or work-up).



### Experimental Section

Melting points were determined on a Kofler block. Ultraviolet spectra were measured on a Unicam Model SP 700 spectrometer and infrared spectra (Nujol) were measured on a Perkin-Elmer Model 257 spectrometer. Mass spectra were recorded on an A. E. I. Model MS 9 spectrometer. Proton magnetic resonance spectra of deuteriodimethyl sulfoxide solutions were taken on a Varian Model A-60A instrument.

**1-( $\alpha$ -Indolyl)-2-( $\beta$ -pyridyl)acrylonitrile (2).**—Nicotinaldehyde, 6 ml, was added to a solution of 8.00 g of  $\alpha$ -indolylacetonitrile<sup>4</sup> and sodium methoxide (from 1.20 g of sodium) in 300 ml of methanol. The mixture was kept at room temperature for 1 hr, diluted with water, and saturated with sodium chloride. The resultant precipitate was filtered and crystallized from acetone, leading in 80% yield to the nitrile **2**: mp 206°; ir (Nujol) 2220  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ );  $\lambda_{\text{max}}$  (EtOH) 270  $\text{m}\mu$  ( $\log \epsilon$  4.14) and 380 (4.46);  $\lambda_{\text{max}}$  (EtOH $_2^+$ ) 269 (4.14) and 389 (4.42);  $\lambda_{\text{max}}$  (EtOH-NaOH) 264 (shoulder, 4.57) and 374 (4.60); mass spectrum  $m/e$  245 ( $\text{M}^+$ ).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{11}\text{N}_3$ : C, 78.35; H, 4.52; N, 17.13. Found: C, 78.23; H, 4.50; N, 16.91.

**6-Cyano-7H-pyrido[3,2-*c*]carbazole (7) and 6-Cyano-7H-pyrido[3,4-*c*]carbazole (8).**—A solution of 600 mg of **2** and 100 mg of iodine in 250 ml of ethanol under nitrogen was irradiated by a high-pressure Hanau Q 81 lamp for 5 hr. Enough sodium thiosulfate was added to decolorize the solution. The mixture was concentrated and then diluted with water. Filtration of the resultant precipitate yielded 520 mg of a solid. Several repetitions of the operation gave 3.80 g of crude product. A solution of the product in a minimum amount of methanol was mixed with 30 g of Florisil (60–100 mesh), the solvent was eliminated, and the remaining powder was added to a chromatography column of 140 g of the same Florisil. The benzene and 100:1 benzene-chloroform eluates led to 275 mg of solid whose crystallization from chloroform gave 150 mg of yellow needles of nitrile **7**: mp >260°;  $\lambda_{\text{max}}$  (EtOH) 222  $\text{m}\mu$  ( $\log \epsilon$  4.52), 250 (4.54), 284 (4.46), 350 (3.95), and 386 (shoulder, 3.74);  $\lambda_{\text{max}}$  (EtOH $_2^+$ )

221 (4.50), 250 (4.50), 282 (4.39), 312 (3.94), 351 (3.85), and 386 (3.74);  $\lambda_{\text{max}}$  (EtOH-NaOH) 250 (4.46), 278 (4.34), 320 (4.25), and 385 (3.82); nmr  $\delta$  7.55 (q, 1,  $J$  = 8, 4.5 cps, H-3), 8.51 (q, 1,  $J$  = 8, 2 cps, H-4), 8.56 (s, 1, H-5), 8.90 (m, 1, H-11), and 9.15 ppm (q, 1,  $J$  = 4.5, 2 cps, H-2); mass spectrum  $m/e$  243 ( $\text{M}^+$ ).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_9\text{N}_3$ : C, 78.99; H, 3.73; N, 17.28. Found: C, 78.80; H, 3.99; N, 17.27.

The chloroform eluates gave a solid whose crystallization from 2:1 chloroform-methanol yielded 1.22 g of yellow crystals of nitrile **8**: mp >260°;  $\lambda_{\text{max}}$  (EtOH) 220  $\text{m}\mu$  (shoulder,  $\log \epsilon$  4.54), 255 (shoulder, 4.54), 271 (4.59), 286 (4.50), and 347 (4.03);  $\lambda_{\text{max}}$  (EtOH $_2^+$ ) 236 (4.47), 260 (4.51), 268 (4.51), and 321 (4.55);  $\lambda_{\text{max}}$  (EtOH-NaOH) 267 (4.49) and 322 (4.65); nmr  $\delta$  7.41 (d, 1,  $J$  = 6 cps, H-1), 8.55 (m, 1, H-11), 8.70 (s, 1, H-5), 8.75 (d, 1,  $J$  = 6 cps, H-2), and 9.41 ppm (s, 1, H-4); mass spectrum  $m/e$  243 ( $\text{M}^+$ ).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_9\text{N}_3$ : C, 78.99; H, 3.73; N, 17.28. Found: C, 78.77; H, 3.89; N, 17.08.

Irradiation of a solution of 500 mg of **2** and 500 mg of ferric chloride in 250 ml of ethanol as above, concentration of the solution, dilution with water and addition of potassium carbonate until the mixture reached pH 6, extraction with chloroform, and further work-up as above gave similar yields of **7** and **8**.

**1,2,3,4-Tetrahydro-3-methyl-6-cyano-7H-pyrido[3,4-*c*]carbazole (9).**—Methyl iodide, 5 ml, was added to a solution of 200 mg of **8** in a minimum amount of methanol and the mixture was kept at 40° for 48 hr. Three additional 5-ml portions of methyl iodide were added during this period. Filtration of the resultant precipitate, 193 mg, and crystallization from methanol yielded **8** methiodide, mp >270°.

*Anal.* Calcd for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{I}$ : C, 52.98; H, 3.11; N, 10.90. Found: C, 52.37; H, 3.12; N, 10.50.

Sodium borohydride, 100 mg, was added in small portions to a suspension of 92 mg of the methiodide in 25 ml of 9:1 methanol-water. The starting material dissolved and the solution assumed a green fluorescence. After 15 min a precipitate appeared. The mixture was diluted with aqueous saturated brine solution and the precipitate, 50 mg, was filtered. Crystallization of the solid from 1:1 methanol-acetone gave the base **9**: mp 250°;  $\lambda_{\text{max}}$  (EtOH) 222  $\text{m}\mu$  ( $\log \epsilon$  4.66), 252 (4.22), 278 (4.35), 306 (4.09), and 364 (3.86);  $\lambda_{\text{max}}$  (EtOH $_2^+$ ) 222 (4.66), 251 (4.44), 277 (4.46), 310 (4.09), and 364 (3.84);  $\lambda_{\text{max}}$  (EtOH-NaOH) 252 (4.28), 278 (4.18), 304 (4.06), and 364 (3.69); nmr  $\delta$  2.38 (s, 3,  $\text{CH}_3$ ), 2.75 (m, 2, C-2  $\text{CH}_2$ ), 3.31 (s, broad, 2, C-1  $\text{CH}_2$ ), and 3.60 ppm (s, broad, 2, C-4  $\text{CH}_2$ ); mass spectrum  $m/e$  261 ( $\text{M}^+$ ), 260 ( $\text{M} - 1$ ), and 218 ( $\text{M} - 43$ ,  $\text{CH}_2=\text{NCH}_3$ ).

*Anal.* Calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3$ : C, 78.13; H, 5.79; N, 16.08. Found: C, 78.10; H, 5.71; N, 15.92.

**1-Cyano-3-( $\beta$ -formylvinyl)carbazole (10a).**—A solution of 600 mg of **2** in 250 ml of ethanol under nitrogen was irradiated by a high-pressure Hanau Q 81 lamp for 15 hr. The solution was concentrated under reduced pressure. Three repetitions of the operation gave 1.80 g of crude product. A solution of the product in a minimum amount of methanol was mixed with 12 g of Florisil (100–200 mesh), the solvent was eliminated, and the remaining powder was added to a chromatography column of 42 g of the same Florisil. The 9:1 benzene-chloroform eluates yielded 405 mg of pure product, while the 4:1 eluates led to 280 mg of somewhat impure material. Sublimation at 150° (0.01 mm) gave **10a**: mp >264°; ir (Nujol) 2230 ( $\text{C}\equiv\text{N}$ ) and 1660  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ );  $\lambda_{\text{max}}$  (EtOH) 213  $\text{m}\mu$  ( $\log \epsilon$  4.61), 309 (4.59), and 346 (4.36);  $\lambda_{\text{max}}$  (EtOH-NaOH) 301 (4.54), 319 (4.56), 354 (shoulder, 4.44), and 438 (4.47); nmr  $\delta$  6.98 (q, 1,  $J$  = 16, 7.5 cps, vinyl  $\beta$  H), 7.85 (d, 1,  $J$  = 16 cps, vinyl  $\alpha$  H), and 9.71 ppm (d, 1,  $J$  = 7.5 cps, aldehyde H); mass spectrum  $m/e$  246 ( $\text{M}^+$ ).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{10}\text{ON}_2$ : C, 78.03; H, 4.09; O, 6.50; N, 11.38. Found: C, 77.68; H, 4.03; O, 6.42; N, 11.12.

**1-Cyano-3-formylcarbazole (11a).**—Osmium tetroxide, 20 mg, was added with stirring to a mixture of 200 mg of aldehyde **10a** in 4 ml of water and 30 ml of dioxane at room temperature. After the dark brown mixture had been left standing for 150 min, 50 mg of sodium periodate was added over a 1-hr period and the mixture was kept at room temperature for 90 min, concentrated under reduced pressure, diluted with water, and extracted with chloroform. The extract was washed with water, filtered twice through 2 g of Florisil, and evaporated. Crystallization of the residue, 165 mg, from methanol yielded aldehyde **11a**: mp 206–208°; ir (Nujol) 2230 ( $\text{C}\equiv\text{N}$ ) and 1680  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ );

(6) The photoinduced hydration of pyridine has been reported: J. Joussot-Dubien and J. Houdard, *Tetrahedron Lett.*, 4389 (1967), and references cited therein.

(7) F. B. Mallory, C. S. Wood and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964), and references cited therein.

$\lambda_{\max}$  (EtOH) 225  $m\mu$  log ( $\epsilon$  4.37), 291 (4.66), and 357 (3.89);  $\lambda_{\max}$  (EtOH-NaOH) 312 (4.45) and 375 (4.00); nmr  $\delta$  8.36 (d, 1,  $J = 2$  cps, H-4), 8.95 (d, 1,  $J = 2$  cps, H-2), and 10.09 ppm (s, 1, aldehyde H); mass spectrum  $m/e$  220 ( $M^+$ ).

Anal. Calcd for  $C_{14}H_{10}ON_2$ : C, 76.36; H, 3.66; O, 7.27; N, 12.72. Found: C, 76.58; H, 3.81; O, 7.55; N, 12.16.

**1-Cyano-3-hydroxymethylcarbazole (11b).**—Reduction of aldehyde 11a followed the procedure for the conversion of 10a into 10b (*vide infra*). Crystallization of the product from 1:1 chloroform-methanol gave 11b: mp 150°;  $\lambda_{\max}$  (EtOH) 222  $m\mu$  (log  $\epsilon$  4.59), 253 (4.31), 278 (4.33), and 366 (3.77);  $\lambda_{\max}$  (EtOH-NaOH) 250 (4.38), 278 (4.36), 294 (shoulder, 4.22), 366 (3.54), and 417 (3.14); mass spectrum  $m/e$  222 ( $M^+$ ).

Anal. Calcd for  $C_{14}H_{10}ON_2$ : C, 75.65; H, 4.54. Found: C, 74.42; H, 4.90.

**1-Cyano-3-( $\beta$ -hydroxymethylvinyl)carbazole (10b).**—Sodium borohydride, 50 mg, was added in small portions to a solution of 50 mg of aldehyde 10a in 15 ml of methanol. After 2 hr the mixture was diluted with water and extracted with chloroform. Evaporation of the extract and crystallization of the residue, 50 mg, from methanol yielded alcohol 10b, mp 204°, mass spectrum  $m/e$  248 ( $M^+$ ).

Anal. Calcd for  $C_{16}H_{12}ON_2$ : C, 77.40; H, 4.87; O, 6.44; N, 11.28. Found: C, 77.28; H, 4.82; O, 6.64; N, 11.39.

Alcohol 10b was acylated by dissolution in a mixture of acetic anhydride and pyridine at room temperature. The usual work-up and crystallization of the crude product from 1:1 acetone-hexane gave acetate 10c, mp 185°.

Anal. Calcd for  $C_{18}H_{14}O_2N_2$ : C, 74.47; H, 4.86; N, 9.65. Found: C, 74.26; H, 4.70; N, 9.56.

**1-Cyano-3-( $\beta$ -carbomethoxyvinyl)carbazole (10e).**—A solution of 200 mg of aldehyde 11a, 160 mg of malonic acid, and a few

drops of piperidine in 8 ml of pyridine was kept at 80° for 1 hr and then at 100° for 2 hr, refluxed for 0.5 hr, and poured into a 10% hydrochloric acid solution. Crystallization of the resultant precipitate, 197 mg, from 3:2 methanol-acetone yielded acid 10d, mp >260°, nmr  $\delta$  6.70 (d, 1,  $J = 16$  cps, olefinic H) and 7.83 ppm (d, 1,  $J = 16$  cps, olefinic H). A solution of 50 mg of the acid and 3 drops of concentrated sulfuric acid in 10 ml of methanol was refluxed for 18 hr and poured into saturated brine solution. Crystallization of the precipitate, 38 mg, from methanol yielded ester 10e, mp 250°, mass spectrum  $m/e$  276 ( $M^+$ ).

Anal. Calcd for  $C_{17}H_{12}O_2N_2$ : C, 73.90; H, 4.38; N, 10.14. Found: C, 73.87; H, 4.20; N, 10.10.

A solution of 30 mg of acid 10d and a few drops of oxalyl chloride in 10 ml of tetrahydrofuran was stirred at room temperature for 90 min. The solvent and excess reagent were evaporated under reduced pressure. The residue was redissolved in 10 ml of anhydrous tetrahydrofuran and mixed with a solution of 20 mg of lithium tri-*t*-butoxyaluminum hydride in 10 ml of tetrahydrofuran. The mixture was stirred at room temperature for 1 hr, diluted with saturated brine solution, and extracted with chloroform. Evaporation of the extract and crystallization of the residue from methanol yielded a crystalline alcohol, identical in all respects with 10b (*vide supra*). Its treatment with acetic anhydride yielded an acetate, identical in all respects with 10c (*vide supra*).

**Registry No.**—2, 22433-55-2; 7, 22433-56-3; 8, 22433-57-4; 8 methiodide, 22433-61-0; 9, 17517-71-4; 10a, 22487-48-5; 10b, 22430-80-4; 10c, 22430-81-5; 10d, 22430-82-6; 10e, 22430-83-7; 11a, 22433-59-6; 11b, 22433-60-9.

## Aziridines. XXII. The Reactions of Some 1-Substituted Aziridines with Carbethoxymethylenetriphenylphosphorane and Carbethoxyethylidinetriphenylphosphorane

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1-Aroylaziridines and related systems have been shown to react with carbethoxymethylenetriphenylphosphorane and carbethoxyethylidinetriphenylphosphorane. The products of reaction arise from intermediates formed by the carbanionic center of the ylide attacking the aziridiny carbon.

Reactions of nucleophiles or reagents possessing nucleophilic sites with either 1-arylaziridines or aziridines bearing other unsaturated 1 substituents have been well studied in recent years.<sup>1-7</sup> The products resulting from these reactions may be rationalized, usually, as arising from intermediates formed by an attack of the nucleophile at the 2 position of the aziridine ring. A new and potentially useful reaction that follows this general pattern, namely, the reaction of 1-arylaziridines and related systems with carbethoxymethylene-triphenylphosphorane (1) and carbethoxyethylidene-triphenylphosphorane (8), has now been observed.

### Results

Carbethoxymethylenetriphenylphosphorane (1) and 1-*p*-nitrobenzoylaziridine in refluxing toluene formed the new and isolable ylide 2 (Scheme I). The structure

of 2 was demonstrated by spectral data and conversion into 4-(*p*-nitrobenzamido)butanoic acid (3). The ir spectrum of 2 showed NH absorption and no carbonyl absorption below 6.15  $\mu$ , evidence that the ester carbonyl group was participating in charge delocalization. Heating of 2 with benzaldehyde and *p*-nitrobenzaldehyde gave the corresponding ethyl 2-benzylidene-4-(*p*-nitrobenzamido)butanoates 4 and 5, respectively, and similar heating of 2 with 2-butenal gave compound 6.

Compound 1 also reacts with 1-*p*-nitrobenzoyl-2-methylaziridine to produce ethyl 4-(*p*-nitrobenzamido)-2-triphenylphosphoranyl-pentanoate (7). Compound 7 was hydrolyzed to 4-(*p*-nitrobenzamido)pentanoic acid. The structure of this acid was authenticated by an alternate preparation involving the reaction of 4-aminopentanoic acid with *p*-nitrobenzoyl chloride and by mass spectroscopy.

Reaction of carbethoxyethylidinetriphenylphosphorane (8) in refluxing toluene formed triphenylphosphine oxide and 1-(*p*-nitrobenzoyl)-2-ethoxy-3-methyl-2-pyrrolone (9) (Scheme II) as well as a small quantity (8%) of 2-*p*-nitrophenyl-2-oxazoline. The structure of

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- (3) P. Thyrum and A. R. Day, *J. Med. Chem.*, **8**, 107 (1965).
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- (5) H. W. Heine and T. Newton, *Tetrahedron Lett.*, 1859 (1967).
- (6) H. W. Heine and M. S. Kaplan, *J. Org. Chem.*, **32**, 3069 (1967).
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