Cyclization of Ylidenemalononitriles. X. Synthesis of Benzazapropellane Derivatives from α-Cyano-β-chloroalkylcinnamonitriles (1a)

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The reaction of nucleophilic and non-nucleophilic bases wtih 2-carbamoyl-3-(γ-chloropropyl)-1-indenone (**5**) have been investigated. Condensation of γ-chlorobutyrophenone with malononitrile afforded α-cyano-β-(3-chloropropyl)cinnamonitrile which was cyclized in concentrated sulfuric acid to produce **5**. Two other products obtained from the cyclization reaction were 2-carbamoyl-3-(γ-chloropropylidene)-1-indanone (**4**) and α-carbamoyl-β-(3-chloropropyl)cinnamamide.

Treatment of a solution of **4** in ethyl acetate with piperidine resulted in cyclization of the γ-chloropropyl side chain to give 2-carbamoyl-3-cyclopropyl-1-indanone. The same compound was obtained in improved yield by the treatment of **4** or **5** with sodium hydroxide solution. The reaction of dimethylamine with **5** in benzene gave initial Michael addition of the amine followed by internal alkylation of the carbanion so formed to yield 3a-dimethylamino-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a(1*H*)carboxamide (**7a**). Similarly addition of ammonia, pyrrolidine, piperidine, benzenethiol, *p*-toluenethiol, 2-naphthalenethiol and nitromethane to the indenone I gave respective analogs of type **7**.

Treatment of **5** with sodium cyanide in aqueous *t*-butyl alcohol resulted in a similar Michael addition followed by internal alkylation. In addition, cyclization between the nitrile and the carbamoyl functions occurred in the same step to give 2-oxo-4-imino-7,8-benzo-3-aza[3.3.3]-propellan-6-one (**13a**). Hydrolysis of the iminopyrrolido ring in **13a** to the corresponding succinimide gave 2,4-dioxo-7,8-benzo-3-aza[3.3.3]propellan-6-one (**13b**). Reaction of **13b** with methyl iodide, allyl bromide, benzyl bromide, and diethylaminoethyl chloride afforded the corresponding *N*-alkylated products. A similar sequence starting with δ-chlorovalerophenone led to 5,6-fused ring systems, including a [4.3.3]propellane. 2,9-Dioxo-4-methyl-7,8-benzo-3-aza[4.3.3]propell-4-ene was obtained by the reaction of **5** with acetone in dilute alkali.

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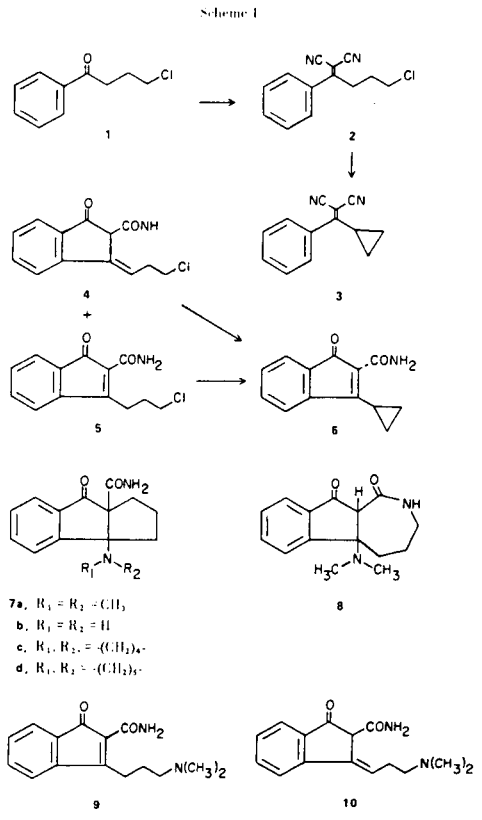
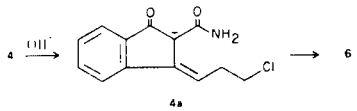
Previous studies in this series (2) have shown that cyclization of β-substituted α-cyanocinnamonitriles usually leads to a mixture of substituted indanones and indenones. The commercial availability of γ-chlorobutyrophenone (**1**) (3) suggests that it could be utilized in this sequence to provide some interesting cyclic ketones bearing a functional group at the 3-position. The chloroketone was readily converted to the corresponding malononitrile **2** by the usual methods. We have already shown that **2**, on treatment with base, was converted to α-cyano-β-cyclopropylcinnamonitrile **3**, (4) a reaction analogous to the conversion of **1** to cyclopropyl phenyl ketone with base, described by Close (5).

Cyclization of **2** in concentrated sulfuric acid in the usual manner (2a) led to a mixture of the white 2-carbamoyl-3-(γ-chloropropylidene)-1-indanone (**4**), bright yellow carbamoyl-3-(γ-chloropropyl)indenone (**5**) and a small amount of non-cyclized diamide, α-carbamoyl-β-(3-chloropropyl)cinnamamide (Scheme 1). The two indones, **4** and **5**, were most conveniently separated by differential solubility in aqueous acid, from which **5** precipitates initially. Apparently **5** is the more stable isomer, since it is obtained in higher yield, and **4** melts to a yellow liquid which on solidification remelts at about the melting point of **5**. Also pure **4** forms a yellow solution in warm alcohol, which contains some **5** by thin film chromatography.

Scheme I



It was hoped that **4** could be converted to a series of 3-dialkylaminoalkylindanones, since compounds of this class have some interesting biological activity (6). However, treatment of **4** with piperidine formed a yellow nonbasic keto-amide, shown to be 3-cyclopropyl-2-carbamoylindenone (**6**) by characteristic infrared (7) and nuclear magnetic resonance (8) for cyclopropyl protons. Compound **6** was obtained in much better yield by warming **4** in dilute sodium hydroxide. The conversion of γ-chloropropyl compounds, such as **2**, to cyclopropyl derivatives involves ionization of a γ-hydrogen, activated in the case of **2** by conjugated cyano groups. The ready conversion of **4** to a cyclopropyl derivative represents a vinylogous reaction which is promoted by the ease of formation of intermediate carbanion **4a**, followed by conjugated elimination of chloride in a homocrotylic E_2' reaction. The



4a

formation of 2-vinyl-1,1-dicarbethoxycyclopropane from δ-bromocrotylmalonic ester in base, reported by Kiersted, Linstead and Weedon (9), is an example of this type of elimination in reverse. Treatment of **5** with strong nonnucleophilic bases, such as sodium hydride, also converted it to **6** in good yield.

Reactions with Nucleophilic Bases.

While the white isomer **4** reacted with amines to produce the cyclopropylindenone **6**, the yellow isomer **5**, 2-carbamoyl-3-(γ-chloropropyl)-1-indenone, followed a different path in reaction with nucleophilic bases. Reaction of **5** with dimethylamine in benzene at room temperature provided a colorless crystalline product. This water-insoluble product failed to show a positive test for chloride with alcoholic silver nitrate. It was soluble in hydrochloric acid and could be reprecipitated by addition of sodium hydroxide solution, showing the presence of the dimethylamine function.

Several structures which fitted the elemental analysis, shown in Scheme 1, were postulated for the product. Simple displacement of chloride would lead to the dimethylaminoalkylindenone **9**, or its valence bond isomer **10**. Structures **9** and **10** were eliminated on the basis of the ultraviolet spectrum of the product, which showed absorption maxima at 206 (ε, 26,320), 246 (ε, 15,600), and 283 nm (ε, 1,900). The general shape of the ultraviolet spectrum was not consistent with the presence of a chromophore such as is present in **2** or **10**, which is seen in the spectrum of **4**, with absorption at 240 (ε, 52,500), 263 (ε, 31,000), 272 (ε, 26,000) and 328 nm (ε, 4,400) or **5**, 247 (ε, 45,500), 253 (ε, 44,200), 328 (ε, 1,500) and 340 nm (ε, 1,400). These spectra are quite similar to those of the corresponding 3-ethyl and 3-ethylidene analogs of **4** and **5**, previously reported (2a).

The ultraviolet spectrum of the product was similar to indanone derivatives containing fused rings (10). Although the ultraviolet spectrum could not distinguish between **7a** and **8**, the infrared spectrum was indicative of **7a**. The infrared spectrum (chloroform solution) of the product showed, among others, a band at 6.35 μ. In the potassium bromide mull spectrum, however, this band moved to 6.24 μ and showed a shoulder at 6.30 μ. These bands, even though shifted out of the normal rnage (11), can best be designated as amide II bands. The presence of an amide II band and the fact that the solution spectrum of the product showed bands at 2.89 μ and 3.61 μ (free NH) indicated the presence of a primary amide group. This was supported by the nuclear magnetic resonances spectrum which very clearly showed two resonances one proton each, centered at δ 8.05 and 6.55 respectively, corresponding to the two protons of the primary amide function. The absence of a peak in the δ 3.2-3.6 region, characteristic of a proton *alpha* in a 1,3-dicarbonyl system (12) also contraindicates structures**8**.

The molecular ion (M) in the mass spectrum of the product (Table I) appeared at m/e 258 with further significant peaks at m/e 215, 197, 186, 171 and 170. High resolution mass spectrometry indicated that the peak of m/e 215 arose by the loss of $CH_3N{=}CH_2$ (mass 43.0422). This peak at m/e 215 was supported by a metastable peak at 179.1.

Table I

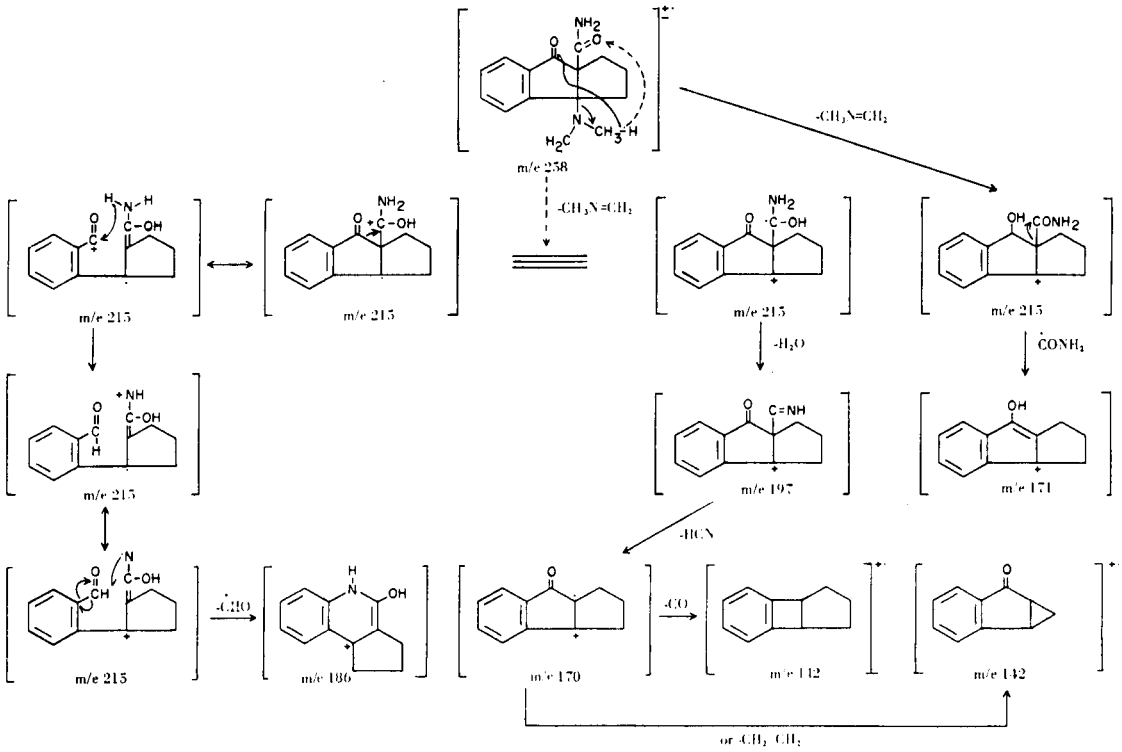
Mass Spectrum of the Dimethylamine Adduct (a)

m/e	relative abundance	m/e	relative abundance
258	24.1	169	11.19
215 (b)	46.2	142	11.53
197	12.48	141	11.71
186	11.79	44	100
171	23.59	43	21.1
170	33.85		

(a) Peaks greater than 10% of the base peak. (b) Exact mass 215.0945; $C_{13}H_{13}NO_2$ requires 215.0946 and $C_{14}H_{17}NO$ 215.1310 (Molecular ion: $C_{15}H_{18}N_2O_2$). Other relevant peaks (relative abundance): 214 (7.79), 198 (5.64), 187 (7.93).

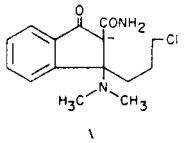
Based on the above data we formulate structure **7a** for the product obtained from the reaction of **5** with dimethylamine. Concerning the loss of fragment $CH_3N{=}CH_2$ in the mass spectrum, molecular models indicate that the methyl protons of the dimethylamino moiety are favorably situated sterically with respect to the amide function to allow for a hydride transfer. The $-C(OH)NH_2$ function so created is then in a position to lose water giving the observed peak at m/e 197. Loss of water (mass 18) from m/e 215 was supported by a metastable peak at m/e

Chart I
Mass Spectral Fragmentation of 7



182.4. Chart I outlines the possible mass spectral fragmentation of **7a**.

The formation of **7a** from **5** probably involves a Michael addition of the amine followed by internal alkylation of the carbanion so formed. Dolfini and Dolfini (13) have constructed piperidine and pyrrolidine rings using a Michael addition-internal alkylation sequence, involving a bifunctional molecule containing both nucleophilic and electrophilic groups and a typical polarized olefin molecule. The nucleophilic group was amino, carbanion or mercapto, and the leaving group was typically halide or tosylate. The reaction of **5** to yield **7a** represents an example of a similar scheme, involving the intermediate carbanion, A.



A

Koelsch (14) studied the Michael addition of anions and carbanions to indenones and reported unsuccessful attempts to alkylate the intermediate anions, formed from 2-carbethoxy-3-phenyl-1-indanone by external alkylating agents. He was able to demonstrate intramolecular alkylation by the addition of phenacyl chloride. Templer (15) has shown that the anion formed during the Michael addition of cyanide to 2-carboxamido-3,4-trimethyleno-1-indenone could be trapped by external alkylating agents such as methyl iodide.

We have extended the Michael addition to **5** to other nucleophiles. Thus the reaction of **5** with ammonia, pyrrolidine and piperidine in benzene gave the expected products **7b-d**. Likewise, the anion of nitromethane, in aqueous *t*-butyl alcohol, gave the expected tricyclic adduct **11a** (Scheme 2). Thiol anions added readily to **5**, producing the corresponding arylthiol adducts **11b-d** in good yield. Compound **11d** was derivatized by dehydration of the amide to a nitrile.

The ready addition of thiol anions prompted us to examine a homolog of **5**, which could be prepared from δ-chlorovalerophenone *via* the corresponding ylidenemalononitrile. Addition of *p*-toluenethiol to 3-δ-chlorobutyl-2-carbamoylindenone produced the 5,6-fused ring compound 4a-(*p*-tolylthio)-1,2,3,4,4a,9a-hexahydro-9a-carbamoylfluorenone (**12**).

Reaction with Cyanide.

The reaction of **5** with sodium cyanide in *t*-butanol afforded a white crystalline compound in high yield. This water-insoluble product was soluble in both dilute hydrochloric acid and dilute alkali. It gave negative Beilstein and alcoholic silver nitrate tests for halogens. That the expected compound **11** (R = CN) was not obtained was indicated by the infrared spectrum which showed no nitrile band: lack of a primary amide was apparent by considerable differences in the carbonyl (5,6-

6.1 μ) and NH (2.9-3.2 μ) stretch regions in the infrared spectra of related compounds (**7a** and **11a**). The molecular weight was consistent with structure **11** (R = CN), but the spectral data indicated further reaction of the cyanide function must have occurred in yielding the product.

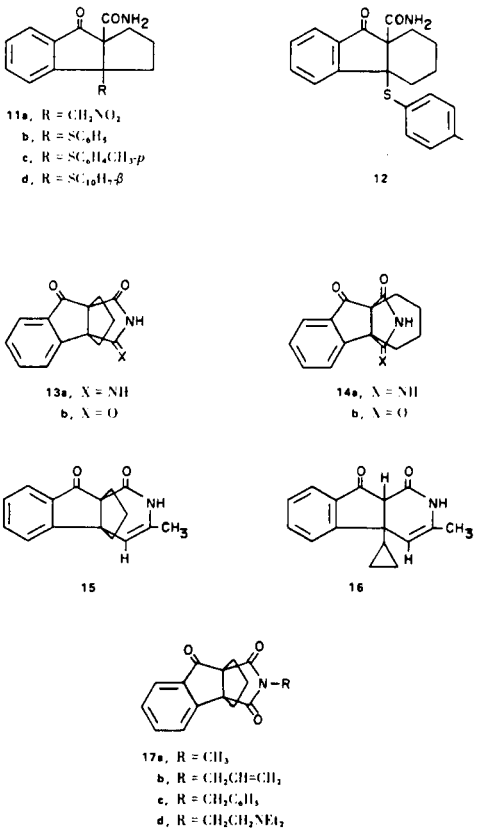
Hydrolysis of the above product with hot dilute phosphoric acid yielded a white crystalline compound which was soluble in dilute alkali but insoluble in water or dilute hydrochloric acid. The structure of this product was shown to be **13b** (2,4-dioxo-7,8-benzo-3-aza[3.3.3]-propellan-6-one (16) by analysis, and chemical and spectral characteristics (Scheme 2). A comparison of the ultraviolet spectral curve of **13b** with that of 3a,4,5,6-tetrahydrosuccinimido[3,4-*b*]acenaphthen-10-ene (17) showed that they were nearly superimposable. Its precursor, **13a**, was formed directly in the alkaline solution by a three step sequence involving addition of cyanide followed by internal alkylation to form the intermediate **11** (R = CN), which is now sterically favored to cyclize again, forming the iminoimide **13a**, a facile cyclization when so favored (10).

In a similar reaction, the imino derivative **14a** was obtained by the addition of cyanide to 3-δ-chlorobutyl-2-carbamoylindenone, and hydrolysis then produced 7,9-dioxo-11,12-benzo-8-aza[4.3.3]propellane-10-one (**14b**).

Another interesting azapropellane derivative was obtained by the addition of acetone anion to **5**, to form 2,9-dioxo-4-methyl-7,8-benzo-3-aza[4.3.3]propell-4-ene (**15**). Since acetone anion was generated *in situ* from a non-nucleophilic base, the isomeric structure (**16**), which could have been formed by initial formation of **6**, followed by Michael addition of acetone and condensation with amide nitrogen, had to be considered. The evidence against **16** came from its nmr spectrum which showed the absence of cyclopropyl protons (δ 0.6) (8) and of the single proton situated alpha to two carbonyl groups in a 1,3-dicarbonyl system (δ 3.3-3.6) (12). The presence of a multiplet (6H) at δ 1.4-2.9 corresponding to the methylenic protons of the cyclopentyl ring favored the structure **15**. Evidence for the unsaturated lactam structure was found in the infrared spectrum, which showed amide CO and NH bands, and the nmr, which showed a methyl group split to a doublet (J - 2CPS) by a *cis* vinyl proton.

Several further examples of the [3.3.3]azapropellane system were obtained by alkylation of **13b**, forming the *N*-substituted derivatives **17a-d** (Scheme 2). Compounds **13a**, **13b**, **14**, and **17a-d**, all succinimide derivatives, were screened for anticonvulsant activity and found to be essentially inactive (18).

Scheme 2



EXPERIMENTAL

Melting points were determined in open capillary tubes in a Mel-Temp heating block apparatus and are corrected. A Perkin-Elmer Model 137 Infracord Spectrophotometer was used to record all spectra in the range 2.5 to 15 μ. Ultraviolet spectra were determined with a Bausch and Lomb Spectronic 505 Recording Spectrophotometer in 95% ethanol. The nuclear magnetic resonance spectra were obtained in deuteriochloroform or specified solvents with a Varian Associates Model A-60 NMR Spectrometer using tetramethylsilane as an internal standard. Chemical shifts are given in parts per million downfield from tetramethylsilane. Coupling constants (J) are given in cycles per second. The abbreviations s, d, t, q, and m indicate singlet, doublet, triplet, quartet, and multiplet, respectively. The nmr data are given by listing the chemical shift, number of protons (when different from that indicated in the assignment), multiplicity, and coupling constants. Mass spectra were obtained with an AEI MS-9 mass spectrophotometer (ionizing energy 70 ev, 100 μA). We are indebted to the National Science Foundation for an instrument grant (GP-5234) for the purchase of the mass spectrometer used in this work. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana.

α-Cyano-β-(3-chloropropyl)cinnamonitrile (**2**).

A mixture of 100 g. (0.55 mole) of γ-chlorobutyrophenone (**1**), (3) 46.25 g. (0.7 mole) of malononitrile, 8 g. of ammonium acetate, 40 ml. of acetic acid, 2.5 ml. of piperidine, and 400 ml. of benzene was refluxed for 20 hours under a Dean-Stark water trap, (the collection of water had ceased after 12 hours). The mixture was allowed to cool, washed with water (3 x 100 ml.), dried and evaporated, yielding 77 g. (61%) of light tan product, m.p. 60-61°. The analytical sample was recrystallized from ethanol-petroleum ether as colorless slabs melting at 61-62°; ir λ max (potassium bromide): 4.5 (C≡N), 6.24 μ (C=C).

Anal. Calcd. for $C_{13}H_{11}ClN_2$: C, 67.68; H, 4.81; N, 12.12. Found: C, 67.50; H, 4.97; N, 12.28.

α-Cyano-β-(4-chlorobutyl)cinnamonitrile.

A mixture of 7.87 g. (0.04 mole) of δ-chlorovalerophenone (prepared by the method of Bordwell and Branner (19)), 13.21 g. (0.2 mole) of malononitrile, 2.0 g. of dry ammonium acetate, 2 ml. of glacial acetic acid, and 250 ml. of 2-propanol was heated under reflux. After 30 minutes, a further portion of ammonium acetate (1 g.) was added and the mixture refluxed gently for 42 hours. The reaction mixture was cooled and the solvent removed under reduced pressure. The resulting dark brown oil was dissolved in chloroform (150 ml.) and the solution washed with water (3 x 70 ml.). The organic layer was dried and evaporated, and the resulting oil was crystallized from ether-hexane to afford 7.67 g. (78.5%) of a pale-yellow solid. Several recrystallizations from ether-hexane gave white prisms, m.p. 45.5-46.2°; ir: λ max 4.48 (C≡N), 6.24 μ (C=C); nmr: (60 Mcps) δ 7.47 (s; aromatic), 3.42 (t, J = 6 cps; Cl-CH_2), 2.95 (t, J = 7.5 cps; C=C-CH_2), and 1.33-2.0 ppm (4H, m; CH_2).

Anal. Calcd. for $C_{14}H_{13}ClN_2$: C, 69.71; H, 5.36; N, 11.45; Cl, 14.48. Found: C, 69.90; H, 5.61; N, 11.56; Cl, 14.32.

Preliminary experiments varying the ratio of ketone to malononitrile from 1:2 to 1:5 resulted in 0.0 to 4.4% of the product. The observation that the yield could be improved to 22% by employing 2-propanol as the solvent and using 1:2 ratio of the ketone to malononitrile, led to the above reaction conditions. Use of β-alanine as catalyst reported by Acker and Hertler (20) to give better yields than ammonium acetate-acetic acid, gave an identical result in the present case.

Sulfuric Acid Cyclization of α-Cyano-β-(3-chloropropyl)cinnamonitrile.

The procedure employed was a modification of that previously reported (2). A solution of 11.54 g. (0.05 mole) of **2** in 150 ml. of concentrated sulfuric acid was kept for 2 hours in an oil bath preheated to 55°. The red solution was cooled to room temperature, poured over 1.3 kg. of crushed ice, and let stand for 1 hour with occasional stirring. The resulting precipitate was collected, washed with water (500 ml.), and dried to yield 7.0 g. of yellow solid. Recrystallization from 2-propanol afforded 4.4 g. (35.2%) of 2-carbamoyl-3-(γ-chloropropyl)indenone (**5**) as brilliant yellow needles, m.p. 128-132°. Repeated recrystallizations raised the melting point to 133-134°; ir: λ max (potassium bromide): 2.91 and 3.14 (NH), 5.86 (ketone carbonyl), 5.95 (amide I), 6.2 and 6.27 μ (C=C and amide II); uv: λ max (nm) 247 (ε, 45,500), 253 (ε, 44,200), 328 (ε, 1,500) and 340 (ε, 1,400); nmr (deuteriochloroform): δ 7.25-7.95 (m; aromatic and NH), 5.7-6.1 (broad; NH), 3.7 (t, J = 6.5 cps; Cl-CH_2), 3.1-3.45 (m; C=CCH_2), 2.0-2.45 ppm (m; CH_2). The product gave a positive 2,4-DNP test.

Anal. Calcd. for $C_{13}H_{12}ClNO_2$: C, 62.53; H, 4.84; N, 5.61; Cl, 14.20. Found: C, 62.81; H, 5.05; N, 5.93; Cl, 14.27.

The above aqueous filtrate was allowed to stand for an additional 4 hours. The resulting precipitate was collected, washed with water (300 ml.) and dried to yield 2 g. (16%) of a pale yellow solid. Recrystallization from 2-propanol gave 1.7 g. of pure white needles, m.p. 161-162°. The white product was identified as 2-carbamoyl-3-(γ-chloropropylidene)-1-indanone (**4**): ir: λ max (potassium bromide): 2.91 (NH), 5.80 (ketone carbonyl), 6.02 (amide I), 6.16 and 6.24 μ (C=C and amide II); uv: λ max (nm) 240 (ε, 52,500), 263 (ε, 31,000), 273 (ε, 26,000), 328 (broad, ε, 4,400). Owing to the low solubility of **4** in the common nmr solvents a spectrum was not obtained. The product gave a positive 2,4-DNP test.

Anal. Calcd. for $C_{13}H_{12}ClNO_2$: C, 62.53; H, 4.84; N, 5.61; Cl, 14.20. Found: C, 62.50; H, 5.04; N, 5.71; Cl, 14.37.

The same aqueous filtrate was now extracted with chloroform (4 x 100 ml.); the chloroform solution was dried and evaporated yielding 0.4 g. (6.9%) of α-carbamoyl-β-(3-chloropropyl)cinnamamide. Recrystallization from 95% ethanol gave white needles, m.p. 149.5-151°; ir λ max (potassium bromide): 3.08 (NH), 6.0-6.24 μ (broad; amide I and amide II); nmr (acetone-d_6): δ 7.35 (s; aromatic), 3.55 (5, J = 8 cps, H_2C=C), and 1.55-1.83 ppm (m; CH_2).

Anal. Calcd. for $C_{13}H_{15}ClN_2O_2$: C, 58.53; H, 5.67; N, 10.51. Found: C, 58.78; H, 5.73; N, 10.67.

Sulfuric Acid Cyclization of α-Cyano-β-(4-chlorobutyl)cinnamonitrile.

A solution of 9.8 g. (0.04 mole) of the title compound in 100 ml. concentrated sulfuric acid was heated for 25 minutes in an oil bath preheated to 57°. A nitrogen atmosphere was constantly maintained over the reaction mixture. The red solution was cooled to room temperature and poured over 1 kg. of crushed ice. After standing for 2 hours with occasional stirring, the resulting precipitate was collected, washed with water (1 l.) and dried to yield 7.35 g. (26.1%) of 2-carbamoyl-3-(δ-chlorobutyl)indenone as brilliant yellow neeldes, m.p. 122-125°. Repeated recrystallizations (2-propanol) raised the melting point to 123.5-125°; ir: λ max 3.04 (NH), 5.87 (ketone carbonyl), 6.02 (amide I), 6.28 μ (broad; C=C and amide II); uv: λ max (nm) 208 (ε, 13,800), 250 (ε, 44,800), 256 (ε, 44,000), 330 (ε, 1,400), 343 (ε, 1,350); nmr (100 Mcps): δ 7.0-8.0 (m; aromatic and NH [broad at 7.78]), 6.05 (broad; NH), 13.56 (t, J = 6 cps; Cl-CH_2), 3.20 (t, J = 6 cps; C=C-CH_2), and 1.6-2.6 ppm (4H, m; CH_2).

Anal. Calcd. for $C_{14}H_{14}ClNO_2$: C, 63.75; H, 5.35; N, 5.31. Found: C, 63.53; H, 5.46; N, 5.50.

The aqueous filtrate was allowed to stand overnight and the resulting precipitate was collected, washed with water (500 ml.) and dried to yield 1.17 g. (11.1%) of a pale yellow solid. Repeated recrystallizations from 2-propanol gave pure white needles, m.p. 149.5-150.5°. The white product turned yellow near the melting point and melted into a yellow liquid. The product showed a strong tendency to turn yellow during recrystallization and even the pure white compound when recrystallized gave a yellow solution. The product was identified as 2-carbamoyl-3-(δ-chlorobutylidene)-1-indanone; ir: λ max 2.93 and 3.02 (NH), 5.80 (ketone carbonyl), 6.01 (amide I), 6.24 μ (amide II).

Anal. Calcd. for $C_{14}H_{14}ClNO_2$: C, 63.75; H, 5.35; mw, 263.0713. Found: C, 63.50; H, 5.42; M^+, 263.0716.

The aqueous filtrate was extracted with chloroform (4 x 70 ml.); the chloroform solution was dried and evaporated yielding 1.09 g. of a yellow solid. Recrystallization from 2-propanol afforded 0.79 g. (7.03%) of an off-white product melting at 150-154°. Repeated recrystallizations gave white needles of α-carbamoyl-β-(4-chlorobutyl)cinnamamide, m.p. 156.6-157.5°; ir: λ max 2.98 (NH), 6.1 (amide I), 6.25 μ (amide II); uv: λ max (nm) 210 (ε, 15,300), 240 (shoulder, inflection point at ε, 6,920).

Anal. Calcd. for $C_{14}H_{17}ClN_2O_2$: C, 59.87; H, 6.10; N, 9.98. Found: C, 59.79; H, 6.30; N, 10.11.

3-Cyclopropyl-2-carbamoylindenone (**6**).

(A). To 5 ml. of 5% sodium hydroxide solution was added 0.5 g. (0.002 mole) of **4**. The white indanone immediately formed a yellow suspension. The reaction mixture was warmed briefly until complete solution occurred, then cooled and acidified, yielding a yellow precipitate which was collected, washed with water (100 ml.) and dried. Recrystallization from methanol afforded 0.32 g. (75%) of long golden needles, m.p. 199-200° dec.; ir λ max (potassium bromide): 3.03 (NH), 3.21 (aromatic and cyclopropyl CH), 5.90 (ketone carbonyl), 6.01 (amide I), 6.24 μ (amide II and C=C); uv: λ max (nm) 210 (ε, 13,800), 255 (ε, 44,160), 261 (ε, 42,320), 280 (ε, 11,200); nmr (pyridine-d_5): δ 6.08-6.98 (m; aromatic), 4.17 (s; H_2O and NH_2), and 0.28-

0.94 ppm (m; cyclopropyl protons). Due to the low solubility of **6** in the nmr solvents (pyridine being best), a poor spectrum was obtained which could not be integrated.

Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; mw, 213.0789. Found: C, 73.07; H, 5.38; M^+, 213.0785.

(B). To a solution of 1.25 g. (0.005 mole) of **4** in 15 ml. of ethyl acetate was added 1 ml. (0.01 mole) of piperidine. The reaction mixture, which had immediately turned yellow, was heated on a steam bath for 1 hour. The precipitated yellow solid was collected, dried, dissolved in chloroform (60 ml.), washed with water (4 x 50 ml.), dried, and evaporated yielding 0.5 g. of a yellow solid. This yellow solid was extracted with hot methylene chloride, the solution filtered, and methylene chloride evaporated to afford 0.20 g. (18.8%) of **6**. Recrystallization from methanol gave long golden needles, m.p. 199-200° dec., identical to **6** by ir and mixed melting point.

(C). A solution of 312 mg. (1.25 mmoles) of **5** in 7 ml. of tetrahydrofuran was treated with 30 mg. (1.25 mmoles) of sodium hydride (60 mg. of 50% suspension in mineral oil). After stirring for 30 minutes, the solution was diluted with water (30 ml.) and acidified. The yellow precipitate (240 mg., 90%) collected and dried, melted at 198-199°, after one recrystallization from methanol. Its ir spectrum was identical to that of pure **6**.

3a-(Dimethylamino)-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a-(1*H*)carboxamide (**7a**).

To 100 ml. of anhydrous, frozen benzene (0°) was added 12.5 ml. (189 mmoles) of liquid dimethylamine. The mixture was stirred and allowed to warm until a slurry was formed. To this slurry was added 0.62 g. (25 mmoles) of **5**, the flask was stoppered and the reaction mixture allowed to stir at room temperature. The benzene solution darkened after 30 minutes and turned dark red within 2 hours. After 74 hours, the solution was concentrated (to *ca.* 5 ml.) and decanted from a light tan precipitate, (dimethylamine hydrochloride) which was extracted with hot benzene (3 x 50 ml.). The combined benzene solution was concentrated (to *ca.* 5 ml.) and allowed to cool to room temperature when pale-green crystals formed (0.25 g.; 38.7%). Crystallization from benzene afforded colorless prisms (0.2 g.), m.p. 169-170°; ir λ max (potassium bromide): 2.98 (NH), 5.98 (carbonyl and amide I), 6.24 μ (C=C and amide II); uv: λ max (nm) 206 (ε, 26,320), 246 (ε, 15,600) and 283 (ε, 1,900); nmr (100 Mcps): δ 8.05 (broad, s; NH), 7.67 (m;; aromatic), 6.55 (broad, s; NH), 1.6-2.8 ppm (m; methyl and methylene protons), methyl protons (s) being at 2.12 ppm. The mass spectrum of **7a** is reported in Table I.

Anal. Calcd. for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.85. Found: C, 69.76; H, 7.01; N, 10.91.

3a-Amino-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a(1*H*)-carboxamide (**7b**).

To 15 ml. of liquid ammonia in a 100 ml. round bottom flask, cooled with a dry ice-acetone bath, was added quickly 1.25 g. (0.005 mole) of **5**. The reaction mixture was refluxed for 1 hour with a dry ice-acetone reflux condenser and then the ammonia was allowed to evaporate slowly to a volume of 5 ml. To the above clear, yellow solution was quickly added 25 ml. of benzene and the flask was stoppered. The frozen reaction mixture was allowed to warm to room temperature and stirred for 24 hours. The solvent was evaporated, the resulting viscous red oil dissolved in 60 ml. of chloroform, washed with water (4 x 30 ml.) and the organic layer dried and evaporated yielding 0.48 g. (41.7%) of a red solid. Repeated recrystallizations from benzene afforded colorless prisms of **7b**, m.p. 155-156°; ir: λ max 2.94 (NH), 5.88 (carbonyl), 5.99 (amide I), 6.24 μ (C=C and amide II); uv: λ max (nm) 210 (ε, 33,840), 251 (ε, 16,900), 294 (ε, 2,725); nmr (100 Mcps): δ 7.3-7.85 (m; aromatic), 6.8-7.2 (1H, broad; CONH), 6.0-6.6 (1H, broad; CONH), and 1.4-2.8 ppm (m; methylene and NH_2 protons).

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17; mw, 230.1055. Found: C, 67.89; H, 6.33; N, 12.20; M^+, 230.1054.

3a-*N*-Pyrrolidino-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a-(1*H*)carboxamide (**7c**).

To a solution of 1.7 ml. (1.42 g.; 0.02 mole) of freshly distilled pyrrolidine in 25 ml. of benzene was added 1.25 g. (0.005 mole) of **5**. The solution, which turned dark red after 30 minutes, was stirred for 44 hours. The solvent was removed and the resulting viscous red oil dissolved in 70 ml. of chloroform, washed with water (4 x 40 ml.), dried, and evaporated to yield 0.72 g. of a viscous red oil. Crystallization from benzene gave 0.33 g. (23.3%) of a yellow solid. Three recrystallizations gave yellow prisms of **7c**, m.p. 200-201°; ir: λ max 2.9 (NH), 5.86 (carbonyl), 5.95 (amide I), 6.26 μ (C=C and amide II); uv: λ max (nm) 209 (ε, 26,000), 250 (ε, 14,000), 288 (ε, 1,740); nmr (60 Mcps): 7.1-8.2 (m; aromatic and NH), 6.3-6.8 (broad; NH), 0.8-3.0 ppm (m; methylene protons).

Anal. Calcd. for $C_{17}H_{20}N_2O_2$: C, 71.80; H, 7.09; N, 9.85; mw, 284.1525. Found: C, 71.88; H, 7.31; N, 9.78; M^+, 284.1525.

3a-Piperidino-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a-(1*H*)carboxamide (**7d**).

To 3 ml. (0.034 mole) of piperidine was added 1.25 g. (0.005 mole) of **5**. The mixture, which had immediately turned red, was stirred at room temperature for 1 hour, then 10 ml. of benzene was added and the stirring continued for 24 hours. The solvent was evaporated and the resulting red oil dissolved in chloroform (70 ml.), and the solution washed with water (4 x 30 ml.), dried and evaporated to yield 1.23 g. of a red oil. Crystallization from benzene afforded 0.43 g. (28.8%) of the product as prisms, m.p. 178-180°. Three recrystallizations afforded pale-yellow prisms of **7d**, m.p. 178-179.5°; ir: λ max 2.90 (NH), 5.87 (carbonyl), 5.94 (amide I), 6.25 μ (C=C and amide II); uv: λ max (nm) 208 (ε, 21,600), 248 (ε, 11,000), 289 (ε, 1,300); nmr (60 Mcps): δ 8.1-8.5 (broad; NH), 7.35-8.0 (m; aromatic), 6.4-6.85 (broad; NH), and 0.9-2.9 ppm (m; methylene protons).

Anal. Calcd. for $C_{18}H_{22}N_2O_2$: C, 72.45; H, 7.43; N, 9.39; mw, 298.1681. Found: C, 72.24; H, 7.36; N, 9.45; M^+, 298.1681.

3a-Nitromethyl-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a-(1*H*)carboxamide (**11a**).

To a solution of 3 g. (0.05 mole) of nitromethane in a mixture of 20 ml. of *t*-butyl alcohol and 5 ml. of 10% sodium hydroxide was added 3 g. (0.012 mole) of **5**. The mixture was allowed to stir for 3 hours, acidified to congo red with 10% sulfuric acid, and diluted with water. The oily layer was decanted and crystallized from benzene-ethanol to afford 1 g. (30%) of light tan prisms, m.p. 180-181°. Three recrystallizations from benzene gave colorless prisms of **11a**, m.p. 183-184°; ir: λ max 2.94 and 3.05 (NH), 5.85 (carbonyl), 5.99 (amide I), 6.27 μ (C=C and amide II); uv: λ max (nm) 209 (ε, 26,400), 252 (ε, 12,500), 293 (ε, 1,860); nmr (60 Mcps): δ 7.15-8.1 (m; aromatic and NH), 5.91 (2H, d, J = 14 cps; NH and $CHNO_2$), 4.92 (d, J = 14 cps; $CHNO_2$), and 0.8-2.6 ppm (m; methylene protons).

Anal. Calcd. for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.15; N, 10.21; mw, 274.0953. Found: C, 60.96; H, 5.40; N, 10.45; M^+, 274.0957.

3a-Phenylthio-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a-(1*H*)carboxamide (**11b**) (21).

To a stirred mixture of 1.50 ml. (excess) of thiophenol in 10 ml. of *t*-butyl alcohol, 0.24 g. of 50% sodium hydride oil dispersion was added. A frothy white solid was immediately formed, and allowed to stir 5 minutes. Then 1.25 g. (5.0 mmoles) of indenone **5** was added, and the system diluted with an additional 5 ml. of alcohol. The yellow color of the indenone gradually faded, and the white precipitate removed by filtration after 30 minutes. Partial evaporation of the mother liquor yielded additional product, giving a total crude yield of 1.70 g. (100%), of m.p. 155-157°. Recrystallization from 2-propanol gave white microcrystals of **11b**, m.p. 162-163.5°; ir: λ max 2.92 (amide N-H), 5.90 (ketone C=O), 5.97 μ (amide C=O).

Anal. Calcd. for $C_{19}H_{17}NO_2S$: C, 70.60; H, 5.31; N, 4.31; S, 9.95. Found: C, 70.41; H, 5.48; N, 4.53; S, 10.22.

3a-*p*-Tolylthio-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a-(1*H*)carboxamide (**11c**) (21).

To a solution of 0.62 g. (5.0 mmoles) of *p*-toluenethiol in 10 ml. of *t*-butyl alcohol was added 0.21 g. (0.005 mole) of 56% sodium hydride oil dispersion. A frothy white solid immediately formed. To this system was added 1.25 g. (0.005 mole) of **5** and 10 ml. of additional alcohol. After 30 minutes stirring, a white solid was collected, m.p. 179-180°; ir: λ max 2.90 (NH), 3.20 (aromatic CH), 5.90 (ketone carbonyl), 6.00 (amide I), 6.26 (amide II), 7.25 μ (methyl).

Anal. Calcd. for $C_{20}H_{19}NO_2S$: C, 71.25; H, 5.64; N, 4.15; S, 9.50. Found: C, 71.22; H, 5.74; N, 4.15; S, 9.43.

3a-(2-Napthylthio)-2,3,3a,8-tetrahydro-8-oxocyclopent[*a*]indene-8a(1*H*)carboxamide (**11d**) (21).

In a typical experiment, 1.60 g. (0.01 mole) of 2-naphthalenethiol was stirred with 2.50 g. (0.01 mole) of **5** and 0.42 g. (0.01 mole) of sodium hydride oil dispersion in *t*-butyl alcohol according to the previously described procedure. Recrystallization of the solid product from benzene yielded 2.90 g. (78%) of **11d**, m.p. 180-182°; ir: λ max 2.90 (NH), 3.30 (aromatic CH), 5.90 shoulder (ketone carbonyl), 6.00 (amide I), 6.23 μ (amide II).

Anal. Calcd. for $C_{23}H_{19}NO_2S$: C, 73.96; H, 5.12; N, 3.75; S, 8.58. Found: C, 73.85; H, 5.13; N, 3.80; S, 8.60.

8a-Cyano-3a-(2-naphthylthio)-2,3,3a,8-tetrahydro-8-oxocyclopent-[*a*]indene (21).

A mixture of 0.33 g. (1.0 mmole) of amide **11d** and 15 ml. of phosphoryl chloride was refluxed for 30 minutes, allowed to cool to room temperature, and poured over 62 g. of ice. When hydrolysis was complete, the aqueous suspension was extracted with ether, the ether extracts washed with water, 5% sodium carbonate, water and dried over anhydrous sodium sulfate. Evaporation of the ether, and drying of the residual solid on a clay plate yielded 0.31 g. (96%) of the 8a-cyano analog of **11d**, m.p. 111-113°. Recrystallization from dilute ethanol yielded 0.25 g. of white needles, m.p. 112-113.5°; ir: λ max 4.45 (CN), 5.80 μ (ketone carbonyl stretch).

Anal. Calcd. for $C_{23}H_{17}NOS$: C, 77.70; H, 4.85; N, 3.94; S, 9.20. Found: C, 77.44; H, 4.81; N, 3.58; S, 9.15.

4a-(*p*-Tolylthio)-1,2,3,4,4a,9a-hexahydro-9-fluorenone-9a(1*H*)carboxamide (**12**) (21).

To a mixture of 0.62 g. (5.0 mmoles) of *p*-toluenethiol and 0.21 g. (0.005 mole) of 56% sodium hydride oil dispersion in 30 ml. of dry dimethylformamide was added 1.32 g. (5.0 mmoles) of 3-δ-chlorobutyl-2-carbamoylindenone and the reaction mixture stirred 4 hours at room temperature. The mixture was then poured over 50 g. of crushed ice, and the resulting white precipitate filtered and recrystallized from benzene yielding 1.50 g. (85.7%) of a white crystalline **12**, m.p. 152-155°. Further recrystallization raised the melting point to 161.5-162.5°; ir: λ max 2.91 (NH), 3.20 (aromatic CH), 5.91 (CO), 6.01 and 6.24 μ (amide I and II).

Anal. Calcd. for $C_{21}H_{21}NO_2S$: C, 74.45; H, 5.98; N, 3.99; S, 9.11; mw 351. Found: C, 74.47; H, 5.72; N, 3.87; S, 8.86; mw (m/e) 351.

2-Oxo-4-imino-6,7-benzo-3-aza[3.3.3]propellan-8-one (**13a**).

A mixture of 7.49 g. (0.030 mole) of 2-carbamoyl-3-(γ-chloropropyl)indenone (**5**), 9 ml. of *t*-butyl alcohol, 30 ml. of water, and 1.62 g. (0.033 mole) of sodium cyanide was heated on a steam bath with frequent swirling. The reaction mixture turned into a clear, brown solution after 2 minutes and further heating for an additional minute produced a white precipitate. The reaction mixture was heated for 15 minutes with constant swirling and allowed to cool to room temperature. The precipitate was filtered and washed with 125 ml. of water to give 6.7 g. (93%) of a white solid, which was soluble in dilute hydrochloric acid and sodium hydroxide. Three recrystallizations from 95% ethanol gave microcrystals of **13a**, m.p. 294-302° dec.; ir: λ max 3.05 (NH), 5.87 (ketone carbonyl), 5.76 and 6.03 μ (asymmetric and symmetric stretch of iminosuccinimide); uv: λ max (nm) 211.5 (ε, 32,960), 235 (ε, 20,560), 299 (ε, 1,425); inflection point at 288 (ε, 1,625). Due to the insolubility of the product in nmr solvents, a spectrum was not obtained.

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.97; H, 5.04; N, 11.66; mw, 240.26. Found: C, 70.21; H, 4.93; N, 11.47; mw, (osmometer, 95% ethanol), 244.

2,4-Dioxo-7,8-benzo-3-aza[3.3.3]propellan-6-one (**13b**).

A solution of 3.60 g. (0.015 mole) of **13a** in 36 ml. of 20% phosphoric acid was refluxed, and a white solid precipitated after an hour. The reaction mixture was refluxed for an additional hour, cooled to room temperature, and the fine, white solid was collected, washed with water (200 ml.) and dried to give 3.61 g. (100%) of the product. Recrystallization from 2-propanol gave microcrystals of **13b**, m.p. 186-187°; ir: λ max 2.75-3.15 (NH), 5.6 (imide asymmetric stretch), 5.9 μ (broad, ketone CO and imide symmetric); uv: λ max (nm) 212 (ε, 18,220), 243 (shoulder, ε, 6,600), 257 (ε, 8,600), and 296 (broad; ε, 1,375); nmr (100 Mcps): δ 8.9 (s, broad; NH), 7.2-7.9 (m; aromatic), and 1.6-2.7 ppm (m; methylene protons).

Anal. Calcd. for $C_{14}H_{11}NO_3$: C, 69.69; H, 4.60; N, 5.80; mw, 241.0739. Found: C, 69.29; H, 4.72; N, 5.90; M^+, 241.0736.

7-Oxo-9-imino-10,11-benzo-8-aza[4.3.3]propellan-12-one (**14a**).

A mixture of 5.27 g. (0.02 mole) of 2-carbamoyl-3-(4-chlorobutyl)indenone, 17 ml. of *t*-butyl alcohol, 50 ml. of water, and 0.64 g. (0.022 mole) of sodium cyanide was heated on a steam bath with frequent swirling. The reaction mixture turned into a clear, brown solution after 2 minutes, and further heating for 30 minutes afforded a white precipitate. The reaction mixture was heated for an additional 30 minutes with constant swirling, cooled and let stand in the refrigerator (6°) for 24 hours. The precipitate was filtered and washed with 200 ml. of water to give 4.35 g. (85.5%) of the product as a white solid, which was soluble in dilute acid and base. Recrystallization from methanol gave microcrystals, m.p. 330-336° dec.; ir: λ max 3.02 (NH), 5.88 (shoulder, ketone carbonyl), 5.78 and 6.08 μ (asymmetric and symmetric stretch of iminosuccinimide); uv: λ max (nm) 211.5 (ε, 8,460), 240 (ε, 5,310), 288 (inflection point, ε, 700); 299 (ε, 525).

Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.87; H, 5.55; N, 11.03. Found: C, 70.74; H, 5.79; N, 11.15.

7,9-Dioxo-11,12-benzo-8-aza[4,3,3]propellan-10-one (**14b**).

A solution of 2.03 g. (0.008 mole) of **14a** in 40 ml. of 20% phosphoric acid was refluxed, and a white solid precipitated after refluxing for 1.5 hours. The reaction mixture was refluxed for 3 hours more, cooled, and stored at 6° for 24 hours. The fine, white solid was collected, washed with water (250 ml.) and dried to afford 1.93 g. (94%) of **14b**. Several recrystallizations from 2-propanol gave microcrystals, melting at 189-190°; ir: λ max 2.9-3.02 (NH), 5.6 (imide asymmetric stretch), 5.8 (shoulder at 5.9 μ, ketone carbonyl and imide symmetric stretch); uv: λ max (nm), 210 (ε, 22,800), 242 (shoulder, ε, 6,960), 257 (ε, 9,500), and 295 (broad, ε, 1,700); nmr (100 Mcps): δ 8.9 (broad, s; NH), 7.3-8.0 (m; aromatic), and 1.2-2.7 ppm (m; methylene protons).

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.64; H, 5.11; N, 6.04.

2,9-Dioxo-4-methyl-7,8-benzo-3-aza[4.3.3]propell-4-ene (**15**).

A mixture of 40 ml. of *t*-butyl alcohol, 30 ml. of acetone, 30 ml. of 10% potassium hydroxide and 6 g. (0.023 mole) of **5** was stirred for 5 hours, diluted with water to 600 ml., and acidified with 85% phosphoric acid. The mixture was allowed to stand overnight and the pale yellow precipitate collected. Two recrystallizations from benzene-ethanol afforded 2 g. (30%) of **15** as colorless prisms, m.p. 262-263°; ir: λ max 2.9 and 3.02 (NH), 5.80 (ketone carbonyl), 5.99 and 6.05 (amide I), 6.24 μ (C=C); uv: λ max (nm) 210 (ε, 33,600), 248 (ε, 12,160), 293 mμ (inflection, point ε, 2,600); nmr (100 Mcps): 7.2-7.85 (m; aromatic and NH), 5.1 (m; C=CH), 1.4-2.9 (m; methylene and methyl protons), 1.93 (d, J = 2 cps, CH_3).

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.88; H, 5.97; N, 5.53; mw, 253.1103. Found: C, 75.58; H, 6.02; N, 5.33; M^+, 253.1103.

2,4-Dioxo-3-methyl-7,8-benzo-3-aza[3.3.3]propellan-6-one (**17a**).

A solution of 4.82 g. (0.02 mole) of **13b** in 100 ml. of dimethylformamide was stirred with 1.96 g. of sodium hydride (50% oil dispersion) at room temperature for 1 hour. To the above solution was added 6.23 ml. (0.1 mole) of methyl iodide and the resulting mixture stirred for 24 hours at room temperature. The reaction mixture was poured over 300 g. of ice, yielding a green-yellow oil, which was extracted with ether (5 x 100 ml.), the ether layer dried and evaporated, and the resulting pale-yellow oil washed with pentane (to remove the mineral oil), and dried under vacuum to give 4.48 g. (88%) of a thick oil. Repeated recrystallization from ether-hexane gave a white solid, m.p. 94-96°; ir: λ max 2.87 (overtone of the band at 5.74 μ), 5.61 (imide asymmetric stretch), 5.79 (ketone carbonyl), 5.89 (imide symmetric stretch), 6.24 μ (C=C); uv: λ max (nm) 211 (ε, 26,800), 241 (shoulder, ε, 7,360), 257.5 (ε, 10,860), 296 (broad, ε, 1,845); nmr (60 Mcps): δ 7.5-8.0 (m; aromatic), 2.96 (s; CH_3), and 1.5-2.84 ppm (m; methylene protons).

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.85; H, 5.39; N, 5.60.

2,4-Dioxo-3-allyl-7,8-benzo-3-aza[3.3.3]propellan-6-one (**17b**).

The method employed was a modification of the procedure of Culberson and Wilder (22) for methylating imides. A mixture of 2.41 g. (0.01 mole) of **13b**, 1.04 ml. (1.45 g., 0.012 mole) of allyl bromide, 2.76 g. (0.02 mole) of potassium carbonate, and 25 ml. of dimethylformamide was stirred at room temperature for 23 hours and poured into 250 g. of ice. The resulting oil was extracted into ether (3 x 75 ml.) and the combined extracts washed with water (3 x 75 ml.), dried, and evaporated to yield 2.57 g. (91.5%) of a pale-yellow solid. Recrystallization from hexane afforded microcrystals of **17b**, m.p. 95.5-98°; ir: λ max 2.85 and 2.9 (overtone), 5.62 (imide asymmetric stretch), 5.75-5.95 (broad; ketone carbonyl and imide symmetric stretch), 6.08 μ (C=C); nmr (60 Mcps): δ 7.4-8.1 (m; aromatic), 5.4-6.0 (1H, m; vinylic proton), 4.8-5.3 (2H, m; vinylic protons), 4.05 (d, J = 6 cps; NCH_2), and 1.65-2.75 ppm (methylene protons).

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.33; H, 5.54; N, 5.15.

2,4-Dioxo-3-benzyl-7,8-benzo-3-aza[3.3.3]propellan-6-one (**17c**).

A mixture of 0.724 g. (3.0 mmoles) of **13b**, 0.48 ml. (4.0 mmoles) of benzyl bromide, 0.415 g. (3.0 mmoles) of potassium carbonate and 10 ml. of dimethylformamide was stirred at room temperature for 22 hours, poured into 100 g. of ice, and the resulting precipitate collected, washed with water (100 ml.) and dried overnight at 60° to afford 1.0 g. (100%) of the product. Recrystallization from hexane gave microcrystals, m.p. 167.5-168.5°; ir: λ max 2.86 (broad; overtone of bands in carbonyl region), 5.6 μ (imide symmetric stretch); nmr (60 Mcps): δ 7.4-7.85 (m; fused aromatic), 7.22 (s; benzyl aromatic), 4.58 (s; CH_2), and 1.67-2.1 ppm (m; methylene protons).

Anal. Calcd. for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23. Found: C, 76.19; H, 5.32; N, 4.24.

2,4-Dioxo-3-diethylaminoethyl-7,8-benzo-3-aza[3.3.3]propellan-6-one (**17d**).

The procedure employed was a modification of the procedure of Voigtlander (23) for dialkylaminoalkylation of active NH and CH compounds. A mixture of 1.30 g. (0.005 mole) of **13b**, 1.03 g. (0.006 mole) of diethylaminoethyl chloride hydrochloride, 1.38 g. (0.01 mole) of potassium carbonate, and 50 ml. of *p*-xylene was refluxed for 17 hours with stirring. The hot xylene solution was filtered and the solvent evaporated under reduced pressure to yield 1.72 g. (100%) of a yellow-brown oil, which was chromatographed on a silica gel column (eluant: 30% benzene-70% ether) to give a colorless oil; ir: λ max 5.6 (imide, asymmetric stretch), 5.79 (ketone carbonyl), 5.88 (imide, symmetric stretch), 6.2 μ (C=C); nmr (60 Mcps): δ 7.5-7.95 (m; aromatic), 3.52 (4H, t, J = 7 cps, NCH_2), 1.7-2.7 (m; methylene protons), and 0.75 ppm (6H, t, J = 7 cps; CH_3). Mw (mass spectrometer; determined on the hydrochloride), found: 340.1784; $C_{20}H_{24}N_2O_3$ requires: 340.1786.

The free amine was converted into its hydrochloride by bubbling anhydrous hydrogen chloride into an ethereal solution of the oil. Several recrystallizations from ethyl acetate-methanol gave white microcrystals, m.p. 172.5-173.5°.

Anal. Calcd. for $C_{20}H_{25}ClN_2O_3$: C, 63.73; H, 6.69; N, 7.43. Found: C, 63.60; H, 6.72; N, 7.54.

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