40 hr, the reaction was cooled and made basic. Extraction with ether afforded 0.37 g (74%) of **1**. The melting point and spectral data were identical with those of commerical samples.

Preparation of (4-Pyridyl)viologen Salts. A. (4-Pyridyl)viologen Nitrate Dihydronitrate (6a).—To 50 ml of water containing 0.7 ml (11 mmol) of concentrated nitric acid was added 0.84 g (2.7 mmol) of **3**. Oxygen was passed through the stirred solution for 5 hr. The solution was concentrated under vacuum to give a brown oil which was recrystallized from water–acetone to yield 0.76 g (52%) of **6a**. The mother solution was concentrated to give a second crop of 0.36 g (24%): mp 178° dec; uv max (H_2O) 286 nm (ϵ 24,300); ir (KBr) 1625 cm^{-1} (viologen salts[7]); nmr (D_2O) τ 1.35 (m, 4), 0.65 (m, 8), 0.15 (m, 4).

Anal. Calcd for $C_{20}H_{18}N_8O_{12}$: C, 42.71; H, 3.23; N, 19.92. Found: C, 42.60; H, 3.41; N, 19.83.

B. (4-Pyridyl)viologen Chloride (6b).—Oxygen was passed through a solution of 0.60 g (6 mmol) of 37% hydrochloric acid and 0.93 g (3 mmol) of **3** in 150 ml of water and 300 ml of acetonitrile. After 24 hr the solution was concentrated under vacuum and the residue was dissolved in 20–30 ml of hot ethanol and 2–3 ml of water. Acetone (10 ml) was added and ether was added to the cloud point. After cooling, 0.60 g (52%) of brown needles of **6b** were obtained: mp 270° dec; ir (KBr) identical with that of **6e** (*vide infra*); uv max (H_2O) 287 nm (ϵ 33,200).

C. (4-Pyridyl)viologen Perchlorate Hydroperchlorate (6c) and Tetraphenylborate (6d).—To 140 ml of 50% aqueous nitromethane containing 10 g (70 mmol) of 70% perchloric acid was added 5.18 g of **3**. Oxygen was passed through the stirred solution for 20 hr. After the solution was concentrated and the resulting water-insoluble precipitate was dried under vacuum, 9.20 g (90%) of crude product was isolated. Recrystallization from water gave 7.65 g (75%) of **6c**, ir (KBr) 1615 cm^{-1} (viologen salts[7]).

Anal. Calcd for $C_{20}H_{17}Cl_3N_4O_{12}$: C, 39.27; H, 2.80; N, 91.7. Calcd for $C_{20}H_{17}Cl_3N_4O_{11}$: C, 40.32; H, 2.88; N, 9.47. Found: C, 40.07; H, 3.28; N, 9.43.

When 1.10 g (2 mmol, assuming a molecular formula of $C_{20}H_{17}Cl_3N_4O_{11}$) of **6c** was dissolved in 60 ml of water at 45°, neutralized with sodium bicarbonate, and treated with 1.50 g (4.37 mmol) of sodium tetraphenylborate in 10 ml of water, 1.80 g (95%) of **6d** was obtained, mp 205–207° dec, ir (KBr) 1630 cm^{-1} (viologen salts[7]).

Anal. Calcd for $C_{68}H_{56}B_2N_4$: C, 85.89; H, 5.94; N, 5.89. Found: C, 85.72; H, 5.96; N, 6.11.

D. (4-Pyridyl)viologen Bromide (6e).—Water (20 ml) containing 0.16 g of 50% aqueous hydrogen bromide (1 mmol) was added to 0.39 g (1 mmol) of (4-pyridyl)viologen cation radical bromide (**7a**) and oxygen was passed through the solution overnight. After concentrating to 5–10 ml under vacuum, a few milliliters of ethanol was added, the solution was warmed, and acetone was added to the cloud point. A small amount of black material was removed by filtration. Additional acetone was added to the warmed solution to yield 0.15 g (32%) of **6e**. Concentration of the filtrate afforded another 0.06 g (13%). The ir spectrum was identical with that of an independently prepared sample.[6b]

When 0.19 g (0.49 mmol) of **7a** and 0.08 g (0.50 mmol) of acid were treated as above and filtered to removed insoluble matter, addition of 0.25 g of sodium tetraphenylborate in 10 ml of water afforded 0.37 g (80%) of **6d**.

Preparation of (4-Pyridyl)viologen Cation Radical Salts. A. (4-Pyridyl)viologen Cation Radical Bromide (7a).—To 50 ml of acetonitrile which had been outgassed with nitrogen for 10 min was added 0.16 g (1 mmol) of bromine and 0.63 g (2 mmol) of **3**. The mixture was stirred under nitrogen for 10 min and chilled in the refrigerator for 15 min, and the blue precipitate was collected by suction filtration. Drying under vacuum gave 0.78 g (99%) of **7a**, mp 200° dec, ir (KBr) 1640, 1580 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}BrN_4$: C, 61.24; H, 4.11; N, 14.28. Found: C, 61.03; H, 4.24; N, 14.28.

B. (4-Pyridyl)viologen Cation Radical Nitrate (7b).—Potassium carbonate (0.12 g, 0.84 mmol) and 0.47 g (0.84 mmol) of viologen nitrate **6a** were dissolved in 20 ml of water. The solution was outgassed with nitrogen for 20 min and 0.10 g (0.41 mmol) of magnesium was added. After stirring under nitrogen for 2 hr, the resulting blue solid was collected by suction filtration and dried under vacuum to afford 0.24 g (78%) of **7b**, mp 220° dec, ir (KBr) 1640, 1580 cm^{-1}.

Anal. Calcd for $C_{20}H_{16}N_5O_3$: C, 64.16; H, 4.31; N, 18.71. Found: C, 63.93; H, 4.51; N, 18.47.

Registry No.—**1**, 553-26-4; **2**, 22752-98-3; **3**, 41764-90-3; **6a**, 41764-91-4; **6b**, 41764-92-5; **6c**, 41764-93-6; **6d**, 41766-78-3; **7a**, 41764-94-7; **7b**, 41764-95-8.

Carbon–Nitrogen *vs.* Nitrogen–Nitrogen Bond Formation in Nitrenoid Cyclization Reactions. Pyrolysis of 3-Azido-4-(2-pyridyl)carbostyrils

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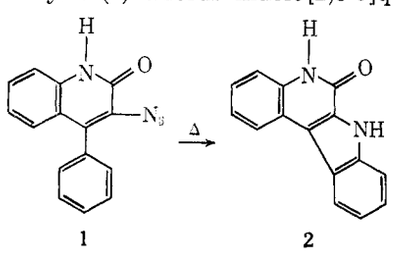
Pyrolysis of 3-azido-4-(2-pyridyl)carbostyrils **7** and **10** afforded mixtures of isomeric tetracyclic products resulting from nitrenoid cyclization reactions. Pyrido[2′,3′:3,2]pyrolo[5,4-*c*]quinolones **9** and **11**, in which the cyclization involved nitrogen–carbon bond formation, were isolated in amounts comparable to those of the pyrido[1′,2′:2,3]pyrazolo[5,4-*c*]quinolones **8** and **12a**, in which the cyclization involved nitrogen–nitrogen bond formation.

Nitrenoid cyclization reactions constitute an important class of reactions for the synthesis of novel heterocyclic compounds.[1] The pyrolysis of 3-azido-4-phenylcarbostyril (**1**) affords indolo[2,3-*c*]quinolone **2** in high yield.[2] In the course of this investigation, we studied the pyrolysis of 3-azido-4-(2-pyridyl)carbostyrils **7**. Related nitrenoid cyclizations of 2-(2-azidophenyl)pyridine,[3] 2-(2-nitrosophenyl)pyridine,[4] and 2-(2-nitrophenyl)pyridine,[3,5] compounds of type **3**, were reported to yield almost exclusively the pyrido[1,2-*b*]indazole (**4**) and not the isomeric δ-carboline **5**.



1 **2**

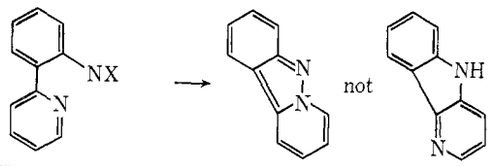
(1) W. Lwowski, Ed., "Nitrenes," Interscience, New York, N. Y., 1970.

(2) (a) J. B. Petersen and K. H. Lakowitz, *Acta Chem. Scand.*, **23**, 971 (1969). (b) We have observed this transformation independently.

(3) R. A. Abramovitch and K. A. H. Adams, *Can. J. Chem.*, **39**, 2516 (1961).

(4) P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).

(5) (a) J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 4831 (1965); (b) J. I. G. Cadogan and R. K. Mackie, *Org. Syn.*, **48**, 113 (1968).



3 (X = N_2, O, or O_2) 4 5

In view of this we anticipated a preference for nitrogen–nitrogen bond formation in the pyrolysis of **7**. It was surprising to find (see Scheme I) that, in addition to nitrogen–nitrogen bond formation (**8**, **12a**), a substantial amount of carbon–nitrogen bond was formed (**9**, **11**). It is this observation that we particularly wish to record.

3-Azido-4-(2-pyridyl)carbostyrils **7** were prepared by the method described[2] for the preparation of 4-phenyl analog **1**. Pyrolysis of **7a** and **7b** in refluxing toluene afforded, in high yields, mixtures which appeared, by tlc, to contain mainly two products. Recrystallizations of these high-melting, highly insoluble mixtures afforded pyrido[1′,2′:2,3]pyrazolo[5,4-*c*]quinolin-6(5*H*)-ones **8a** and **8b** in 35 and 52% yields, respectively. The second product was not isolated but was presumed to be 5,7-dihydropyrido[2′,3′:3,2]pyrolo[5,4-*c*]quinolin-6-(5*H*)-ones **9**. In order to prove the presence of the isomers **9** in the mixture of pyrolysis products, we peralkylated the crude mixture with 2-diethylaminoethyl chloride in the presence of sodium hydride. The monoalkylated products **12**, formed from **8**, could be readily separated from the dialkylation products of **9**, compounds **13**, which were isolated as dihydrochlorides.

Alternately, the 3-azidocarbostyril **7a** was alkylated first. The 1-(2-diethylaminoethyl) derivative **10** was pyrolyzed, without isolation, to afford a mixture of the two isomeric cyclization products **11** and **12a** which were isolated in 17 and 36% yields, respectively.

Structural assignments are based on nmr, ir, and uv spectral data. The two isomeric heterocyclic nuclei have clearly different uv spectra. The characteristically sharp and strong NH stretching band (3200 cm^{-1}) in the ir spectrum of **11** is consistent with that expected for the NH of ring-fused pyrroles.[6]

Experimental Section[7]

2-(2-Azidoacetamido-5-bromobenzoyl)pyridine.—Sodium azide (15.3 g, 236 mmol) was dissolved in a hot solution of 47.0 g (118 mmol) of 2-(5-bromo-2-bromoacetamidobenzoyl)pyridine (**6b**)[8] in 1.6 l. of methanol. The solution was heated to gentle reflux on a steam bath for 20 min. Methanol was evaporated. The residue was extracted with boiling hexane. The hot hexane solution was decanted through a plug of cotton. This process was repeated until only insoluble salts remained. The combined hexane extracts afforded, on cooling and concentration, 31.0 g (73%) of yellow needles: mp 102–103°. (after recrystallizations from hexane, the melting point rose to 103–104°); ir (KBr) 2100 cm^{-1} (N_3); nmr (DMSO-d_6) δ 3.74 ppm (s, 2 H, CH_2); uv max (EtOH) 239 nm (ϵ 27,600) and 343 (2750).

Anal. Calcd for $C_{14}H_{10}BrN_5O_2$: C, 46.69; H, 2.80; N, 19.44. Found: C, 46.71; H, 3.00; N, 19.13.

3-Azido-4-(2-pyridyl)carbostyril (7a).—To a hot solution of 79.8 g (0.25 mol) of 2-(2-bromoacetamidobenzoyl)pyridine[11] (**6a**) in 1.2 l. of methanol was added in one portion 32.5 g (0.50 mol) of sodium azide. The mixture was heated on a steam bath to a slow reflux for 20 min. As the solution partially cooled to room temperature, 0.33 mol of benzyltrimethylammonium hydroxide (13.6 ml of a 35% methanolic solution) was added, and the mixture was left to stand at room temperature overnight. The crystals formed (51.0 g, 80%) were collected by filtration and washed thoroughly with methanol. The product was pure by tlc. An analytical sample was prepared by recrystallization from ethanol to give yellow needles: melting point indefinite (decomposition between 100–140° indicated by a change in color from yellow to white); ir (KBr) 2100 (N_3) and 1645 cm^{-1} (CO); uv max (EtOH) 230 nm (ϵ 30,070), 304 (12,490), 326 (10,160), 339 (12,660), and 354 (9420).

Anal. Calcd for $C_{14}H_9N_5O$: C, 63.87; H, 3.45; N, 26.60. Found: C, 64.04; H, 3.51; N, 26.49.

3-Azido-6-bromo-4-(2-pyridyl)carbostyril (7b). A.—To a warm solution of 3.00 g (8.34 mmol) of 2-(2-azidoacetamido-5-bromobenzoyl)pyridine in 150 ml of methanol was added 1.0 ml of a 35% solution of benzyltrimethylammonium hydroxide in methanol. The solution was allowed to stand at room temperature. After 20 hr, the fibrous yellow solid (2.24 g, 79%) was collected and washed thoroughly with methanol. It was pure by tlc. During melting point determination decomposition was indicated by color change in the range 115–130°, giving a high-melting residue. An analytical sample was prepared by recrystallization from ethanol: uv max (EtOH) 215 nm (ϵ 23,950), 240 (33,100), 294 (10,800), 304 (12,000), 345 (11,100), 360 (8900).

Anal. Calcd for $C_{14}H_8BrN_5O$: C, 49.15; H, 2.36; N, 20.47; Br, 23.35. Found: C, 49.33; H, 2.58; N, 20.37; Br, 23.47.

B.—Alternately, the product was obtained in 97% yield directly from the bromoacetamido precursor **6b**[8] without isolation of the intermediate azide. Thus after 96.0 g (241 mmol) of 2-(2-bromoacetamido-5-bromobenzoyl)pyridine and 31.2 g (480 mmol) of sodium azide were heated in 3.2 l. of methanol for 20 min, 16 ml of 35% solution of benzyltrimethylammonium hydroxide in methanol was added to the partially cooled mixture. In two crops, 80 g of **7b** was collected.

Pyrido[1′,2′:2,3]pyrazolo[5,4-*c*]quinolin-6(5*H*)-one (8a), 5-(2-Diethylaminoethyl)pyrido[1′,2′:2,3]pyrazolo[5,4-*c*]quinolin-6-(5*H*)-one (12a), and 5,7-Bis(2-diethylaminoethyl)-5,7-dihydropyrido[2′,3′:3,2]pyrolo[5,4-*c*]quinolin-6(5*H*)-one (13a) Dihydrochloride.—A suspension of 13.2 g (50 mmol) of azidocarbostyril **7a** in 500 ml of toluene was heated under reflux for 3 hr. The crystalline product mixture that separated from solution was collected and washed with toluene (12.5 g). Tlc (silica gel, ether) of this material indicated a clean mixture of two products appearing at R_f 0.08 and 0.35. After drying *in vacuo*, the entire solid mixture was suspended in 1.2 l. of dry dimethylformamide containing 7.20 g of a 50% dispersion of sodium hydride (0.30 mol) in mineral oil. After stirring for 0.5 hr at room temperature, 0.160 mol of 2-diethylaminoethyl chloride (50 ml of a 3.20 *M* solution in toluene) was added and stirring was continued for 3 hr. Excess hydride was decomposed with water; solvents were evaporated. The residue was partitioned between methylene chloride and water. The methylene chloride layer was dried (Na_2SO_4) and evaporated. Trituration of the residue with ether afforded 6.50 g of **12a** as a light brown powder, mp 123–125°. Recrystallization from acetonitrile afforded 4.2 g (25%) of colorless prisms: mp 124–126°; ir (KBr), no NH band, 1665 cm^{-1} (CO); uv max (*i*-PrOH) 215 nm (ϵ 34,600), 228 sh (27,000), 236 (26,600), 249 (35,700), 257 sh (30,000), 266 sh (18,500), 292 sh (6200), 305 (9600), 319 sh (12,900), 330 (14,800), 351 sh (8850), 368 sh (5300); nmr ($CDCl_3$) δ 1.05 (t, J = 7 Hz, 6, 2 CH_2CH_3), 2.65 (q, J = 7 Hz, 4, 2 CH_2CH_3), 2.80 (m, 2, CH_2N), 4.50 (m, 2, CH_2NCO), 6.90–7.40 (m, 5, aromatic), 7.80–8.35 (m, 2, aromatic), 8.72 ppm (d, J = 7 Hz, 1, aromatic).

(6) A. R. Katritzky and A. P. Ambler in A. R. Katritzky, Ed., "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press, New York, N. Y., 1963, p 208.

(7) All melting points were taken in capillaries heated in oil baths and are corrected. Infrared spectra were determined on a Beckman IR-9 or a Perkin-Elmer 621 grating spectrometer, nuclear magnetic resonance spectra on a Varian A-60 or a Varian HA-100 spectrometer, using tetramethylsilane as internal standard unless specified otherwise, and ultraviolet spectra with a Cary 14M or 15 recording spectrometer. Solvents used were of reagent grade purity. All solvents were evaporated on a Büchi Rotavapor evaporator under water-aspirator pressure using a water bath heated to 30–80°.

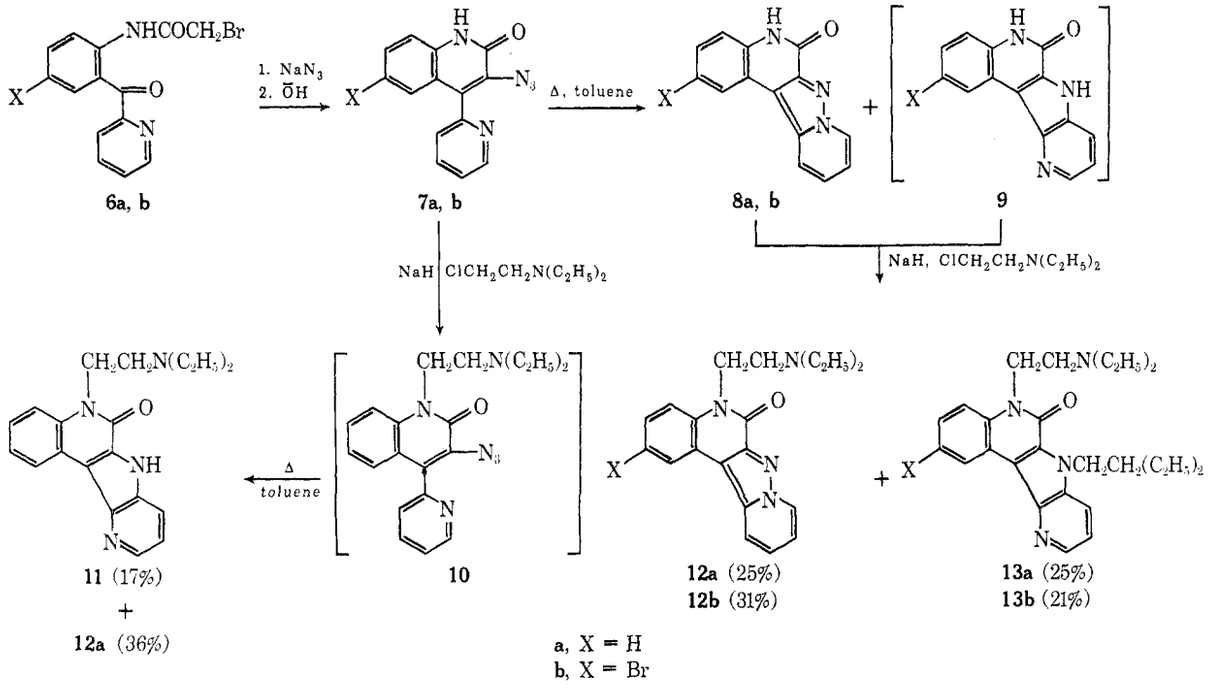
(8) This compound (mp 105–107°) was prepared by the bromoacetylation of 2-(2-amino-5-bromobenzoyl)pyridine,[9,10] following essentially the same procedure as described for **6a** in ref 9.

(9) R. I. Fryer, R. A. Schmidt, and L. H. Sternbach, *J. Pharm. Sci.*, **53**, 264 (1964).

(10) L. O. Randall, W. Schallek, L. H. Sternbach, and R. Y. Ning in "Psychopharmacological Agents," Vol. III, M. Gordon, Ed., Academic Press, New York, N. Y., in press.

(11) This compound (mp 117–119°) was prepared as described in ref 9.

Scheme I



Anal. Calcd for $C_{20}H_{22}N_4O$: C, 71.83; H, 6.63; N, 16.76. Found: C, 72.10; H, 6.95; N, 16.84.

The ethereal mother liquors were evaporated to dryness. The residual oil was dissolved in a minimum of ethanol, and to the solution was added an excess of 4 *M* ethanolic hydrogen chloride. The precipitated hydrochloride salt was collected by filtration. Recrystallizations from methanol–ether afforded 6.50 g (25%) of the dihydrochloride salt of **13a** as colorless needles: mp 276–277°; ir (KBr) 1653 cm^{-1} (CO); uv max (CH_3OH) 232 nm (ε 38,500), 351 (26,600), 257 (27,100), 274 sh (9320), 310 (13,600), 317 sh (12,500), 334 sh (8400), 348 (10,900), 364 (9320); nmr (D_2O, external TMS) δ 1.83 and 1.87 (2 t, J = 7 Hz, 6 each, 4 CH_2CH_3), 3.88 [m, 12, 2 $CH_2N(CH_2)_2$], 4.91 and 5.48 (2 m, 2 each, CH_2NCO and CH_2NCCO), 7.65–8.10 (m, 3, aromatic), 8.18–8.46 (m, 2, aromatic), 8.98 ppm (2 d, J = 7 Hz, 1 each, aromatic).

Anal. Calcd for $C_{26}H_{35}N_5O \cdot 2HCl \cdot H_2O$: C, 58.85; H, 7.53; N, 13.20. Found: C, 58.78; H, 7.73; N, 13.17.

Alternately, the crude pyrolysis product mixture of **7a** from toluene was recrystallized thrice from dimethylformamide. Compound **8a** was obtained as colorless needles in 35% yield: mp above 325°; ir (Kbr) 3100–3200 (weak bands, amide NH) and 1670 cm^{-1} (CO); uv max (*i*-PrOH, above 240 nm) 253 nm (ε 29,500), 263 sh (17, 700), 304 sh (8400), 318 sh (11,900), 329 (13,750), 350 sh (8400), 368 sh (4700).

Anal. Calcd for $C_{14}H_9N_3O$: C, 71.48; H, 3.86; N, 17.86. Found: C, 71.70; H, 3.92; N, 18.00.

2-Bromopyrido[1′,2′:2,3]pyrazolo[5,4-*c*]quinolin-6(5*H*)-one (8b), 2-Bromo-5-(2-diethylaminoethyl)pyrido[1′,2′:2,3]pyrazolo-[5,4-*c*]quinazolin-6(5*H*)-one (12b), and 2-Bromo-5,7-bis(2-diethylaminoethyl)-5,7-dihydropyrido[2′,3′:3,2]pyrolo[5,4-*c*]quinolin-6(5*H*)-one (13b) Dihydrochloride.—A suspension of 70.9 g (0.207 mol) of azidocarbostyril **7b** in 3.5 l. of toluene was heated to reflux for 6 hr. The crystalline product mixture that separated from solution was collected and washed with toluene (62.1 g). Tlc (silica gel, ether) of this material indicated a relatively clean mixture of two products appearing at R_f 0.09 and 0.39. This mixture was alkylated in the same manner as described in the preparation of **12a** and **13a**, using 3 l. of dimethylformamide, 24.0 g of 50% dispersion of sodium hydride (1.0 mol) in mineral oil and 0.80 mol of 2-diethylaminoethyl chloride (250 ml of a 3.20 *M* solution in toluene). Crystallization of the product mixture from acetonitrile followed by recrystallizations from the same solvent afforded 26.5 g (31%) of **12b** as colorless needles: mp 194–197°; ir (KBr) 1667 cm^{-1} (CO); uv max (*i*-PrOH) 221 nm (ε 32,350), 233 sh (27,400), 245 sh (33,750), 251 (39,200), 263 sh (25,000), 270 sh (21,200), 317 sh (12,500), 331 (16,450), 350 (11,550), 366 (7750); nmr ($CDCl_3$) δ 1.06 (t, 6, 2 CH_2CH_3), 2.69 (q, 4, 2 CH_2CH_3), 2.76 (m, 2, CH_2N), 4.46 (m, 2, CH_2NCO), 7.05–7.55 (m, 4, aromatic), 8.00–8.16 (m, 2, aromatic), 8.75 ppm (d, J = 7 Hz, 1, aromatic).

Anal. Calcd for $C_{20}H_{21}BrN_4O$: C, 58.12; H, 5.12; N, 13.56. Found: C, 58.25; H, 5.03; N, 13.54.

The acetonitrile mother liquors were combined and evaporated to dryness. The residue was dissolved in a minimum of ethanol and treated with an excess of 4 *M* ethanolic hydrogen chloride. After standing, the precipitated hydrochloride salt was collected and washed with ethanol. After recrystallizations from ethanol, the dihydrochloride salt of **13b** was obtained as yellow needles (25.5 g, 21%): mp 255–258°; ir (KBr) 1650 cm^{-1}; uv max (CH_3OH) 240 nm (ε 47,500), 253 sh (25,500), 261 (23,600), 270 sh (14,750), 279 (11,100), 303 sh (9750), 311 (12,950), 318 sh (11,300), 336 sh (8950), 349 (12,400), 366 (11,000); nmr (D_2O, external TMS) δ 1.86 and 1.90 (2 t, 6 each, 4 CH_2CH_3), 3.86 [m, 12, 2 $CH_2N(CH_2)_2$], 4.66 and 5.34 (m, 2 each, CH_2NCO and CH_2NCCO), 7.43 (d, J = 9 Hz, 1, H-4), 7.75 (d of d, J = 2 and 9 Hz, 1, H-3), 7.94 (d of d, J = 5 and 9 Hz, 1, H-9), 8.31 (d, J = 2 Hz, 1, H-1), 8.54 (d, J = 9 Hz, 1, H-8), 8.78 ppm (d, J = 5 Hz, 1, H-10).

Anal. Calcd for $C_{26}H_{34}BrN_5O \cdot 2HCl$: C, 52.99; H, 6.20; N, 11.96. Found: C, 53.00; H, 6.11; N, 11.81.

Alternately, the crude pyrolysis product mixture of **7a** from toluene was recrystallized from dimethylformamide–ethanol. Compound **8b** was obtained as colorless needles in 52% yield: mp above 350°; ir (KBr) 3175 and 3080 (medium, amide NH) and 1680 cm^{-1} (CO); uv max (EtOH–1.6% DMF) 247 nm (ε 40,000), 257 sh (26,000), 265 sh (21,200), 318 sh (13,400), 330 (17,250), 347 sh (12,400), 363 sh (8000).

Anal. Calcd for $C_{14}H_8BrN_3O$: C, 53.58; H, 2.57; N, 13.38; Br, 25.44. Found: C, 53.30; H, 2.59; N, 13.33; Br, 25.06.

5-(2-Diethylaminoethyl)-7*H*-pyrido[2′,3′:3,2]pyrolo[5,4-*c*]-quinolin-6(5*H*)-one (11) and 5-(2-Diethylaminoethyl)pyrido-[1′,2′:2,3]pyrazolo[5,4-*c*]quinolin-6(5*H*)-one (12a).—A mixture of 5.20 g (20.0 mmol) of 3-azido-4-(2-pyridyl)carbostyril (**7a**), 1.20 g of a 50% dispersion in oil of sodium hydride (50 mmol), and 50 ml of dimethylformamide was stirred for 0.5 hr. To this mixture was added 10 ml of a 3.20 *M* toluene solution of 2-diethylaminoethyl chloride (32 mmol). After stirring for 3 hr, the excess hydride was decomposed with water and the solvent evaporated. The residue was partitioned between methylene chloride and water. The methylene chloride layer was dried (Na_2SO_4) and evaporated to dryness.

The residue was dissolved in 100 ml of toluene and heated to reflux for 5 hr. Evaporation of toluene followed by crystallizations from acetonitrile afforded 1.10 g (17%) of 11 as colorless needles: mp 253–255°; ir (KBr) 3200 (sharp and strong, NH) and

1630 cm^{-1} (CO); uv max (*i*-PrOH) 233 nm (44,750), 250 (28,750) 257 (28,400), 274 sh (10,500), 308 sh (14,300), 314 (15,000), 342 (10,550), 357 (8550).

Anal. Calcd for $C_{20}H_{22}N_4O$: C, 71.83; H, 6.63; N, 16.75. Found: C, 71.93; H, 6.87; N, 16.85.

The acetonitrile mother liquors were combined and evaporated to dryness. Trituration of the residue with ether afforded a light brown amorphous solid, which on recrystallizations from acetonitrile gave 2.40 g (36%) of **12a** as colorless prisms, mp 122–125°. This material was found to be identical with **12a** obtained above by tlc and comparison of infrared spectra.

The separation of **11** and **12a** were aided by tlc analyses. On silica gel plates developed in a mixture (1:1) of ethanol and ethyl acetate, **11** appeared at R_f 0.22 and **12a** at R_f 0.08.

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Registry No.—**6a**, 41526-19-6; **6b**, 1694-64-0; **7a**, 41895-15-2; **7b**, 41895-16-3; **8a**, 41895-17-4; **8b**, 41895-18-5; **11**, 41895-19-6; **12a**, 41895-20-9; **12b**, 41895-21-0; **13a** dihydrochloride, 41895-22-1; **13b** dihydrochloride, 41895-23-2; 2-(2-azidoacetamido-5-bromobenzoyl)pyridine, 41895-24-3.

Reaction of Polyarylated Carbinols. IV. Reactions of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol with Sodium Amide. Effect of Quenching Temperature on the Products Obtained

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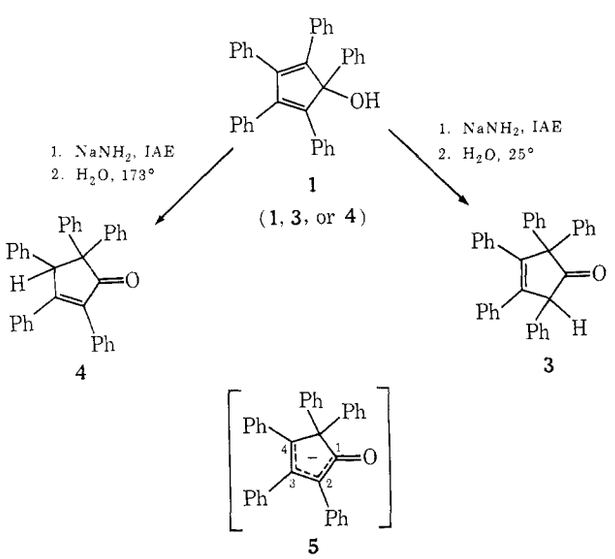
The reaction of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) with catalytic and equimolar amounts of sodium amide has been observed and its mechanism investigated. With catalytic amounts of sodium amide the reaction of **1** has been observed to occur *via* the same mechanism previously reported with other bases. With equimolar amounts of sodium amide 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1), 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**3**), and 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (**4**) are all observed to produce exclusively **3**, the kinetically controlled product, if quenched with water at room temperature, and **4**, the thermodynamically controlled product, if quenched with water at 173°. A mechanism for production of these products involving initial formation of **3** in each case is proposed. Reaction of the anion formed when **1** is treated with equimolar amounts of sodium amide and quenched with benzoyl and benzyl chloride at both room temperature and at 173° is also discussed.

During our continuing study[1-3] of reactions of polyarylated carbinols we have observed[3] that heating 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (**1**)[4,5] to 173° in isoamyl ether (IAE) in the presence of bases such as sodium hydroxide afforded a mixture of isomeric kinetically and thermodynamically controlled ketones, 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**3**)[6,7] and 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (**4**),[6] respectively.

We now wish to report the results of this rearrangement when it is performed in the presence of sodium amide and offer some mechanistic explanation for the differences observed.

Treatment of dienol **1**, ketone **3**, or ketone **4** at 173° in IAE with 1 molar equiv of sodium amide followed by cooling of the anion solution to room temperature and quenching with water produces exclusively ketone **3**, the kinetically controlled product. However, if the anion solution is prepared in exactly the same manner from either dienol **1**, ketone **3**, or ketone **4**, but is quenched at 173° with water, ketone **4**, the thermodynamically controlled product, is exclusively produced.

While these results with molar equivalents of sodium amide are different from the results obtained with sodium hydroxide,[3] the results obtained (Table I, Experimental Section) when catalytic amounts of sodium amide are used as base (molar ratio of 10 dienol **1**:1 $NaNH_2$) are identical with those obtained in the reaction of the dienol **1** in IAE with sodium hydroxide as the base.[3] Thus in the reaction of dienol **1** with catalytic amounts of sodium amide, the products formed are obtained by internal quenching and *via* the same mechanism previously described[3] for the sodium hydroxide catalyzed reaction.



This mechanism does not, however, apply in the case where equimolar amounts of sodium amide are employed. Since this quantity of base ensures complete

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