Calcd for $C_{21}H_{19}FO_8$: C, 60.03; H, 4.55. Found: C, 59.96; H, 4.65.

Methyl 4,7-tetrahydro-3-methyl-4,7-etheno-2aH-cyclopent-[*b*,*c*]indene-1,2,5,6-tetracarboxylate (XIII) was recrystallized from aqueous methanol, mp 106–107.5°. *Anal.* Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.96; H, 5.26.

Registry No.—Indene, 95-13-6; I, 7646-55-1; II, 7635-37-2; VI, 7635-30-3; VIII, 7646-56-2; IX, 7646-57-3; X, 7646-58-4; methyl 1,2,2a,3,4,5,6,7,8,9-decahydro-3,5a-methano-5aH-cyclobuta[*d*]naphthalene-1,2,4,5-tetracarboxylate, 7635-39-4; XII, 7635-40-7; XIa, 7695-31-0; XIb, 7646-59-5; XIc, 7635-41-8; XId, 7646-60-8; XIII, 7706-43-6.

Acknowledgments.—We wish to express appreciation for the interest and help of Dr. E. Schlittler throughout this work. Mr. F. LeMunyon carried out the vapor phase chromatography and Dr. J. Marsh helped with nomenclature problems. Microanalyses were performed under the supervision of Mr. G. Robertson. The mass spectrum was run by Dr. H. Hürzeler, CIBA Ltd., Basle, Switzerland.

Synthesis of Azaindenes. The Benzo[*c*]pyrazolo[1,2-*a*]cinnolinium Cation, a Novel Heteroaromatic Cation[1]

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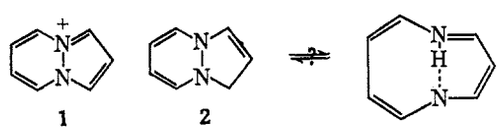
Investigation of possible synthetic routes to the pyrazolo[1,2-*a*]pyridazinium cation (**1**) and the potentially aromatic 1,5-diazonene (**3**) has led to the observation of a novel reaction of benzocinnoline and trimethylene dibromide, the preparation of a novel dibenzoderivative **7** of **1**, and the observation of a mild aromatization reaction involving loss of either hydrogen atoms or a methyl group. The 1,3-dipolar addition reaction has been applied to the synthesis of a number of azaindenes.

The work to be described was initially undertaken to examine the synthesis and the properties of derivatives of pyrazolo[1,2-*a*]pyridazinium cation (**1**) and its dihydro derivative (**2**). These systems were considered to be of interest because of their novelty, the unusual ten π-electron cationic system present in **1**, and the possibility of valence and prototropic tautomerism of **2** to the potentially aromatic ten π-electron monocyclic heterocycle 1,5-diazonene (**3**).[3] We report



1 **2** **3**

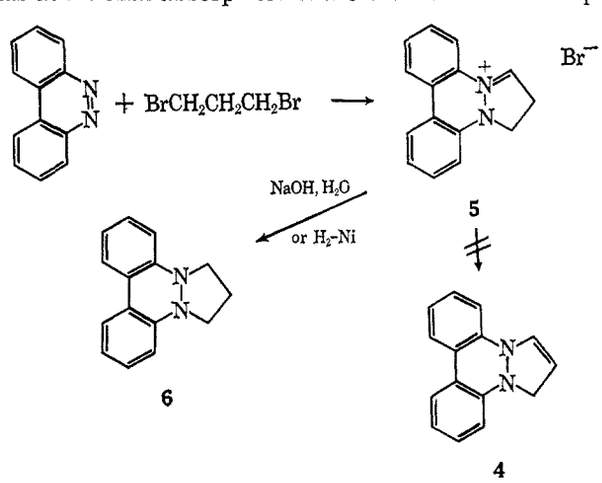
here some preliminary, and partially successful efforts to prepare derivatives of **1** and **2**.

Our first goal was the dibenzo derivative (**4**) of **2**. Reaction of benzocinnoline with trimethylene dibromide in boiling ethanol gave a good yield of dark red, felted needles, no melting point below 290°, identified as the imminium bromide **5** (2,3-dihydrobenzo[*c*]-pyrazolo[1,2-*a*]cinnolinium bromide) on the basis of the following evidence. The ionic nature of the compound was evident by formation of blood-red solutions in water which gave an immediate precipitate with silver nitrate. Analysis was in accord with the structure. The infrared spectrum was completely free from N–H absorption from 2.5 to 4.0 μ. The ultraviolet–visible spectrum is compared with that of benzocinnoline N-oxide in Table I. It can be seen that the major regions of ultraviolet absorption overlap for these two related systems, although red bromide **5** has additional absorption in the visible. It was hoped

TABLE I

ULTRAVIOLET AND VISIBLE SPECTRA OF BENZOCINNOLINE AND SOME ANALOGS

$\lambda_{max}^{95\% EtOH}$, m$\mu$ (log ϵ)				
5	Benzocinnoline N-oxide	**7**	**6**	Benzocinnoline
222 (4.08)	245 (4.48)	218 (4.11)	253 (3.55)	251 (4.70)
259 (4.69)	253 (4.50)	259 (4.74)	317 (3.36)	308 (3.95)
295 (3.76)	265 (4.30)	293 (3.81)	392 (3.42)	372 (3.20)
320 (3.70)	285 (4.00)	319 (3.72)		
333 (3.72)	330 (3.95)	333 (3.72)		
373 (2.87)	365 (3.80)			
391 (3.11)			415 (2.54)	
487 (2.53)				
528 (2.53)			525 (1.54)	



that treatment of red bromide **5** with base would result in conversion to the desired eneamine (**4**). However, from the addition of aqueous sodium hydroxide to an

(1) This investigation was supported by Public Health Service Research Grant GM 12383-02 from the Division of General Medical Sciences.

(2) Fellow of the Alfred P. Sloan Foundation, 1962–1965. Department of Chemistry, Michigan State University, East Lansing, Mich. 48823.

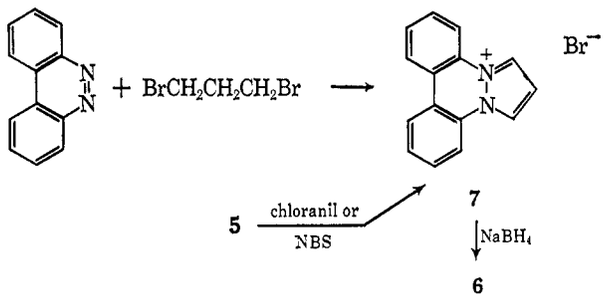
(3) Several recent examples of heterocyclic[4] and carbocyclic[5] relatives of **1** and **2** have appeared in the literature.

(4) (a) T. W. G. Solomons, F. W. Fowler, and J. Calderazzo, *J. Am. Chem. Soc.*, **87**, 528 (1965); (b) V. Boekelheide and N. A. Fedoruk, *Proc. Natl. Acad. Sci. U. S.*, **55**, 1385 (1966).

(5) (a) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).

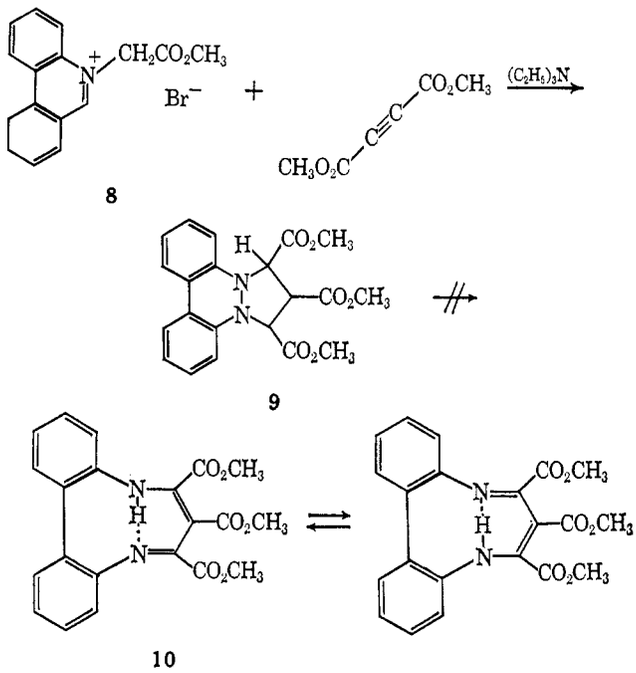
aqueous solution of **5**, only orange *dihydro* derivative **6** (48%) could be isolated. The same dihydro derivative (**6**) could be isolated in 68% yield by catalytic hydrogenation of **5** over Raney nickel in water. The structure of orange dihydro compound **6** was evident from its analysis, the absence of NH absorption in its infrared spectrum, and the similarity of its ultraviolet spectrum to that of benzocinnoline (see Table I). As in red bromide **5**, the unusual π system present in **6** was evident in its visible absorption.[6]

The observation of the formation of **6** suggested a facile disproportionation of eneamine **4** and red bromide **5** and prompted a search for the other possible disproportionation product, the benzo[c]pyrazolo[1,2-a]-cinnolinium cation (**7**). This ion was readily synthesized as its bromide salt by dehydrogenation of red bromide **5** with either chloranil in dimethyl sulfoxide or N-bromosuccinimide in chloroform, or by direct reaction of benzocinnoline with 1,2,3-tribromopropane in boiling ethanol.



The bromide salt of aromatic cation **7** was isolated as white needles, no melting point below 290°. It was insoluble in hydrocarbon solvents, but dissolved readily in water and gave an immediate precipitate with aqueous silver nitrate. Its infrared spectrum was free from NH absorption, while its ultraviolet spectrum was remarkably similar to that of red bromide **5** (see Table I), lacking the absorption in the visible characteristic of **5**. The nmr exhibited a two-proton doublet at τ 1.5, assigned to the proton α to nitrogen, and a nine-proton multiplet at 3.18 for the remaining protons. The compound could be reduced with sodium borohydride to orange dihydro compound **6**, thereby further correlating the structures of the several compounds.

We then turned to another route for the synthesis of derivatives of **2**. The success of Huisgen's 1,3-dipolar additions[8] suggested their application here. Thus, reaction of the methyl bromoacetate adduct of benzocinnoline (**8**) with dimethyl acetylenedicarboxylate resulted in the formation of a deep orange, crystalline compound. The expected structure (**9**) for this product is in accord with its infrared absorption at 5.70 and 5.85 μ for the saturated and unsaturated ester functions, the absence of NH absorption, and its nmr spectrum, in which the methyl ester functions are evident as three sharp singlets at τ 6.04, 6.18, and 6.27 (areas 3:3:3), the methine proton as a sharp singlet at 4.45 (area 1), and the aromatic protons as a broad multiplet near 2.7 (area 8). The alternative macrocyclic tautomer of **9**, 2,3,4-tricarbomethoxy-6,7,8,9-dibenzo-1,5-diazonene (**10**), was ruled out as the structure of this product by the appearance in the nmr of a sharp methine resonance at τ 4.45, and three different methyl resonances. The ester functions at positions 2 and 4 in diazonene **10** would be expected to appear equivalent in the nmr by fast proton exchange between the nitrogens. There was no evidence for the presence of **10** in the unchanged nmr spectrum of samples of **9** which had been boiled in xylene for 18 hr.



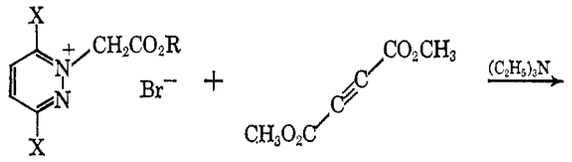
The failure of adduct **9** to exhibit any tendency to rearrange to dibenzodiazonene **10** caused us to turn attention to less highly substituted derivatives of 1,5-diazonene. To that end we examined the 1,3-dipolar addition reaction of the pyridazine–methyl bromoacetate adduct (**11**, R = CH_3, X = H) with dimethyl acetylenedicarboxylate. Instead of the desired mode of addition, however, the reaction provided dimethyl-fumarate and the dehydrogenated product, 5,6,7-tricarbomethoxypyrrolo[1,2-b]pyridazine (**12**, R = R′ = CH_3; X = H), identified by its analysis, spectra, and the correspondence of its melting point with the literature value.[9] The preparation of this product had been reported by reaction of pyridazine and dimethyl acetylenedicarboxylate.[9] In order to establish that its origin in the present work was the 1,3-dipolar addition reaction, the 1,3-dipolar addition of pyridazine–ethyl bromoacetate adduct (**11**, R = C_2H_5; X = H) was carried out with dimethyl acetylenedicarboxylate. The product from this reaction appeared to be the expected 5,6-dicarbomethoxy-7-carbethoxypyrrolo[1,2-b]-pyridazine (**12**, R = C_2H_5; R′ = CH_3; X = H) from its analysis, infrared spectrum (5.75, 5.85, and 5.95 μ), and nmr spectrum, which exhibited the characteristic ethyl group resonances (τ 5.54, quartet; 8.59, triplet; areas 2:3) in place of the highest field methyl resonance of **12** (R = R′ = CH_3, X = H). A mechanistically feasible alternative (**12**, R = CH_3; R′ = C_2H_5; X = H) is not ruled out but is considered less likely.

(6) Although the origin of the intense red color of bromide **5** is not clear, a referee has pointed out that other deeply colored, not too distantly related quarternary cations have been noted previously.[7]

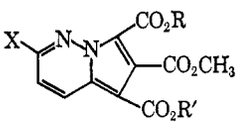
(7) M. J. Perkins, *J. Chem. Soc.*, 3005 (1964); H. Paul and A. Weise, *Tetrahedron Letters*, 163 (1963).

(8) R. Huisgen, *Angew. Chem., Intern. Ed. Engl.*, **2**, 633 (1963).

(9) R. L. Letsinger and R. Lasco, *J. Org. Chem.*, **21**, 764 (1956).



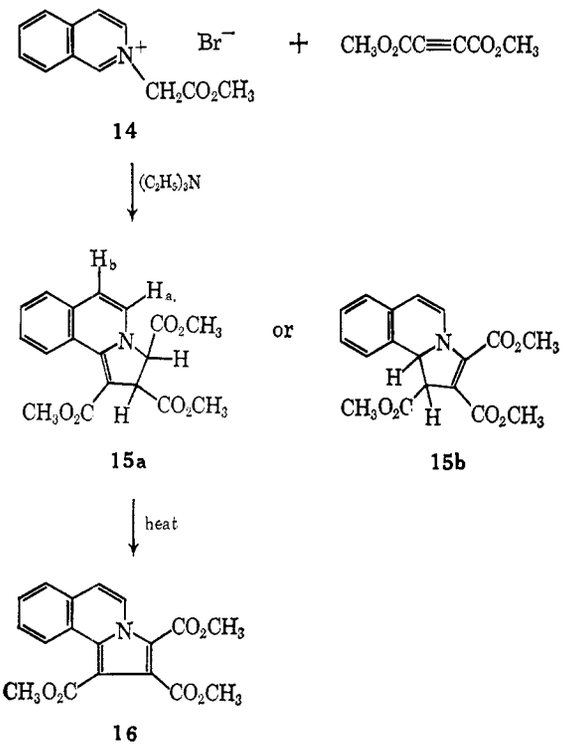
11



12

In an effort to block aromatization to products of type **12**, the same sequence of reactions was carried out with 3,6-dimethylpyridazine–methyl bromoacetate adduct (**11**, R = X = CH_3). Surprisingly, in spite of the mild conditions of this reaction (triethylamine in boiling methylene chloride), a methyl group was lost with the formation of the aromatic 2-methyl-5,6,7-tricarbomethoxypyrrolo[1,2-*b*]pyridazine (**12**, R = R′ = X = CH_3). The structure assigned to this product is compatible with its elemental analysis and spectra, as well as the correspondence of its melting point with that recorded in the literature.[9]

In a further investigation of this facile aromatization reaction, the adduct of isoquinoline and methyl bromoacetate (**14**) was treated with dimethyl acetylenedicarboxylate and triethylamine. Two crystalline products were isolated from the reaction mixture. One of these, obtained as yellow cubes, turned out to be the primary adduct (**15a** or **15b**), and by heating at its melting point or by simply boiling in methanol, could be dehydrogenated in high yield to the other, isolated as colorless needles, identified as dehydro compound **16**.



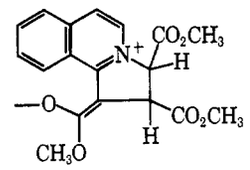
14

15a

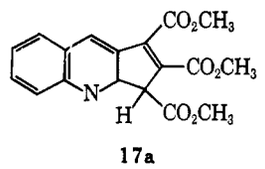
15b

16

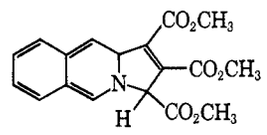
The presence of two less hydrogens in **16** was evident from analytical data and mass spectra of the two compounds. Thus **15** exhibited a "parent peak" in its mass spectrum at *m/e* 343, while that of **16** appeared at *m/e* 341. The expected infrared carbonyl absorption of **15** appeared at 5.73 and 5.95 μ, while that of **16** appeared at 5.73, 5.77, and 5.83 μ. The nmr spectrum of **15**, in addition to exhibiting other expected resonances, established the adjacency of the two saturated hydrogens, appearing at τ 4.69 and 5.57, by their 13-cps coupling. Although either **15a** or **15b** is compatible with these observations, **15a** is favored on the basis of the greater stability expected for its quinolinoid system (as in resonance contributor **15c**), and the comparably long wavelength, high-intensity ultraviolet absorption of **15** and the aromatic **16** (see the Experimental Section). Isomeric structures, **17a** or **17b** and **18** for these products are ruled out by the appearance of two doublets (J = 8 cps) in the nmr spectrum of **15** (τ 3.51 and 4.15) corresponding to H_a and H_b, as well as the already noted coupling between the saturated hydrogens. Compound **16** has been twice reported as the product of the reaction of isoquinoline and dimethyl acetylenedicarboxylate.[10] Our melting point and ultraviolet data are in satisfactory agreement with the literature values.



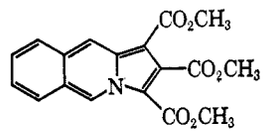
15c



17a



17b



18

Experimental Section

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected unless otherwise stated. All boiling points are uncorrected. A Perkin-Elmer Infracord was used for recording infrared spectra. Ultraviolet spectra were taken on a Cary Model 14. A Varian A-60 spectrometer was used for obtaining the nmr spectra, using tetramethylsilane or tetramethylammonium fluoroborate (τ 6.87) as an internal standard.[11] Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Benzo[*c*]cinnoline.—This material was prepared from 2,2′-dinitrobiphenyl (Aldrich 19,560) in 95% yield following the procedure of Badger, Seidler, and Thomson.[12] The pale yellow crystals had mp 157° (lit.[12] 156°), λ_{max}^{KBr} 6.2 and 6.35 μ.

2,3-Dihydrobenzo[*c*]pyrazolo[1,2,-*a*]cinnolinium Bromide (5).—A solution of benzo[*c*]cinnoline (10.0 g, 0.056 mole) and 1,3-dibromopropane (59.5 g, 0.3 mole) in absolute ethanol (100 ml) was boiled under reflux for 80 hr. Filtration of the cooled mixture yielded blood-red crystals (11.3 g, 68%). Recrystallization

(10) R. M. Acheson and I. Hole, *J. Chem. Soc.*, 748 (1962); R. H. Wiley and L. H. Knabeschuh, *J. Org. Chem.*, **18**, 836 (1953); we are grateful to a referee for calling these references to our attention.

(11) In recording the nmr spectra the following procedure will be used: for example τ 1.5 (2 H, d). The H refers to the integrated area under the peak equivalent to the number of protons indicated. The second letter in parentheses refers to the multiplicity of the peak, *i.e.*, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Thus, the example indicates a doublet centered at τ 1.5 equivalent to two protons.

(12) G. M. Badger, J. H. Seidler, and B. Thomson, *J. Chem. Soc.*, 3207 (1951).

from absolute ethanol provided an analytical sample (80% recovery) as blood-red crystals, which did not melt below 290°.

Anal. Calcd for $C_{15}H_{13}BrN_2$: C, 59.83; H, 4.35; Br, 26.53; N, 9.30. Found: C, 60.08; H, 4.22; Br, 26.34; N, 9.13.

2,3-Dihydro-1H-benzo[c]pyrazolo[1,2-a]cinnoline (6). A. From 5 and Sodium Hydroxide.—An aqueous solution (25 ml) of red bromide salt **5** (2.0 g, 0.007 mole) was treated with 10% aqueous sodium hydroxide until the red color disappeared. The mixture was stirred for several hours, then filtered yielding an orange solid (0.7 g, 48%, mp 189–192°). Recrystallization from absolute ethanol gave analytically pure orange needles: mp 194–194.5°; λ_{max}^{KBr} 6.25, 6.7, and 6.75 μ.

Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.11; H, 6.45; N, 12.85.

B. Catalytic Hydrogenation of 5.—A mixture of red bromide salt **5** (5.0 g, 0.017 mole) and Raney nickel (2.5 g) in water (250 ml) was hydrogenated at 3 atm for 5 hr. The reaction mixture was filtered and the catalyst was washed thoroughly with methylene chloride. The aqueous layer was extracted several times with methylene chloride (200 ml) and the methylene chloride solutions were combined. After drying over anhydrous potassium carbonate, the solvent was removed *in vacuo*. The orange, crystalline product (2.5 g, 68%) had a melting point (195°) and infrared spectrum identical with those of the product prepared by method A.

C. From Benzo[c]pyrazolo[1,2-a]cinnolinium Bromide (7) and Sodium Borohydride.—To a stirred ice cold solution of the salt benzo[c]pyrazolo[1,2-a]cinnolinium bromide (**7**, 1.0 g, 0.0033 mole, *vide infra*) in water (30 ml) and methylene chloride (50 ml) was added dropwise an ice-cold solution of sodium borohydride (0.05 g, 0.0013 mole) in water (50 ml). The methylene chloride layer turned yellow during the addition. After stirring for 1 hr and separation, the methylene chloride solution was dried over anhydrous potassium carbonate. Evaporation of the solvent *in vacuo* left an orange, crystalline solid (0.3 g, 90% based on available hydride). The infrared spectrum and melting point (195°) of this material were identical with those of product **6** prepared from red bromide salt **5**.

Benzo[c]pyrazolo[1,2-a]cinnnolinium Bromide (7). A. From Red Bromide Salt 5 and Chloranil.—A solution of red bromide salt **5** (2.0 g, 0.007 mole) and chloranil (6.0 g, 0.027 mole) in dry dimethyl sulfoxide (75 ml) was boiled under reflux for 2 hr. The solution was then cooled and the excess chloranil was removed by filtration. The boiling under reflux was continued for 2 additional hr, then the mixture was cooled and dry ether (75 ml) was added. The buff precipitate (0.87 g, 44%) was recrystallized from absolute ethanol providing an analytical sample as white needles (75% recovery) with no melting point below 290°; λ_{max}^{KBr} 6.6, 7.0, 7.5, and 13.0 μ; nmr (D_2O) τ 1.5 (2 H, d) and 3.18 (9 H, m).[11]

Anal. Calcd for $C_{15}H_{11}BrN_2$: C, 60.25; H, 3.68; Br, 26.75; N, 9.37. Found: C, 60.15; H, 3.86; Br, 26.89; N, 9.43.

B. From Red Bromide Salt 5 and N-Bromosuccinimide.—To a solution of red bromide salt **5** (4.0 g, 0.013 mole) in chloroform (200 ml) was added N-bromosuccinimide (3.0 g, 0.017 mole). The mixture was boiled under reflux for 3 hr, cooled, and then filtered. The solid residue (4.5 g) was recrystallized from methanol providing buff needles (1.85 g, 46%). The infrared spectrum of this sample was identical with that of the product prepared by procedure A.

Anal. Calcd for $C_{15}H_{11}BrN_2$: C, 60.25; H, 3.68; Br, 26.75; N, 9.37. Found: C, 60.08; H, 3.74; Br, 26.72; N, 9.60.

C. From Benzo[c]cinnoline and 1,2,3-Tribromopropane.—A mixture of benzo[c]cinnoline (10.0 g, 0.055 mole) and 1,2,3-tribromopropane (45.0 g, 0.16 mole) in absolute ethanol (110 ml) was boiled under reflux for 168 hr. The solution was cooled and dry ether added until the turbidity persisted. Filtration gave a buff powder (9.5 g, 58%), whose infrared spectrum was identical with that of the products from methods A and B.

Anal. Calcd for $C_{15}H_{11}BrN_2$: C, 60.25; H, 3.68; Br, 26.75; N, 9.37. Found: C, 59.97; H, 3.90; Br, 26.14; N, 9.33.

N-(Carbomethoxymethyl)benzo[c]cinnolinium Bromide (8).—A solution of benzo[c]cinnoline (3.0 g, 0.017 mole) and methyl α-bromoacetate (3.0 g, 0.02 mole) in methylene chloride (30 ml) was heated briefly on a steam bath. The mixture was then stored in the cold, and after 2 days the crystalline mass was removed by filtration. Recrystallization of the orange crystals (4.10 g, 74%, mp 160–165°) from methanol–ether provided an analytical sample: mp 164–166°; 80% recovery; λ_{max}^{KBr} 5.75, 7.0, 8.15, and 13.0 μ.

Anal. Calcd for $C_{15}H_{13}BrN_2O_2 \cdot 0.5H_2O$: C, 52.6; H, 4.20; Br, 23.4; N, 8.20. Found: C, 52.95; H, 4.20; Br, 23.62; N, 8.26.

1,2,3-Tricarbomethoxy-1-H-benzo[c]pyrazolo[1,2-a]cinnoline (9).—To a solution of N-(carbomethoxymethyl)benzo[c]cinnolinium bromide (**8**, 2.0 g, 0.006 mole) and dimethyl acetylenedicarboxylate (2.5 g, 0.0176 mole) in methylene chloride (50 ml) boiling under reflux was added dropwise a solution of triethylamine (3.0 g, 0.03 mole) in methylene chloride (25 ml). The addition took approximately 30 min. The boiling under reflux was continued for 5.5 hr after the addition of the triethylamine solution. After cooling, the reaction mixture was washed once with water (50 ml) and dried over anhydrous potassium carbonate. After removal of the solvent *in vacuo*, methanol (25 ml) was added to the residue. The methanol solution was heated, filtered, and allowed to cool slowly. The orange, crystalline product (2.1 g, 89%, mp 187–188°) was recrystallized from methanol providing an analytical sample: mp 187–188°; λ_{max}^{KBr} 5.70, and 5.85 μ; nmr ($CDCl_3$) τ 6.04 (3 H, s), 6.18 (3 H, s), 6.27 (3 H, s), 4.45 (1 H, s), and 2.7 (8 H, m).

Anal. Calcd for $C_{21}H_{18}N_2O_6$: C, 63.95; H, 4.60; N, 7.10. Found: C, 63.89; H, 4.64; N, 7.16.

Pyridazine (XI). A. From 3,6-Dichloropyridazine.—Catalytic hydrogenation of 3,6-dichloropyridazine (Aldrich D 7320) over 10% Pd-C catalyst according to the procedure of Mizzoni and Spoerri[13] provided pyridazine in 55% yield, bp 89° (14.5 mm) [lit.[13] 86–87° (14 mm)].

B. From 2,5-Dimethoxy-2,5-dihydrofuran.—Sulfuric acid hydrolysis of 2,5-dimethoxy-2,5-dihydrofuran (Aldrich D 13, 410) and subsequent reaction with hydrazine hydrate according to the method of Letsinger and Lasco[9] yielded pyridazine in a 70% yield, bp 89° (14.5 mm).

N-(Carbomethoxymethyl)pyridazinium Bromide (11, X = H, R = CH_3).—The adduct, prepared in the usual way (see above), from pyridazine (5.5 g, 0.069 mole) in methylene chloride (60 ml) and methyl α-bromoacetate (11.0 g, 0.072 mole) was obtained crude as a yellow, crystalline solid (14.6 g, 91.3%), mp 130–135°. Recrystallization from methanol–ether provided an analytical sample: mp 138–140°; 87% recovery; λ_{max}^{KBr} 5.80 μ; nmr (D_2O) τ 0.66 (2 H, m), 1.66 (2 H, m), 4.5 (2 H, s), and 6.5 (3 H, s).

Anal. Calcd for $C_7H_9BrN_2O_2$: C, 36.05; H, 3.90; Br, 34.28; N, 12.01. Found: C, 35.82; H, 4.10; Br, 34.01; N, 12.06.

5,6,7-Tricarbomethoxypyrrolo[1,2-b]pyridazine (12, X = H; R = R′ = CH_3).—A solution of N-(carbomethoxymethyl)-pyridazinium bromide (**11**, X = H; R = CH_3) (4.0 g, 0.017 mole) and dimethyl acetylenedicarboxylate (8.0 g, 0.056 mole) in methylene chloride (100 ml) was boiled under reflux. A solution of triethylamine (6.0 g, 0.059 mole) in methylene chloride (50 ml) was added dropwise over 45 min. The mixture was boiled under reflux for an additional 4 hr.

The reaction mixture was then cooled and washed once with water (75 ml). The methylene chloride solution was then dried over anhydrous potassium carbonate; the solvent was removed by rotary evaporation. The gummy residue was sublimed at 50° (2 mm) and the white crystals which sublimed out were removed and identified by infrared spectroscopy and melting point as dimethyl fumarate.

The nonsublimable residue was taken up in hot methanol (50 ml) and allowed to cool slowly. Filtration yielded pale yellow crystals (3.9 g, 78.5%, mp 163°) (lit.[9] 160–161°). Recrystallization from methanol gave an analytical sample with unaltered melting point; λ_{max}^{KBr} 5.79, and 5.90 μ; nmr ($CDCl_3$) τ 1.5 (2 H, m), 3.0 (1 H, m), 6.0 (3 H, s), 6.1 (3 H, s), and 6.2 (3 H, s).

Anal. Calcd for $C_{13}H_{12}N_2O_6$: C, 53.43; H, 4.13; N, 9.59. Found: C, 53.43; H, 4.15; N, 9.55.

N-(Carbethoxymethyl)pyridazinium Bromide (11, X = H; R = C_2H_5).—The adduct, prepared in the usual way from pyridazine (5.0 g, 0.0625 mole) and ethyl α-bromoacetate (11.0 g, 0.066 mole) in methylene chloride (60 ml), was isolated crude as a tan, crystalline solid (13.1 g, 85%), mp 164–168°. Recrystallization from ethanol–ether gave an analytical sample: mp 167–169°; λ_{max}^{KBr} 5.85 μ; nmr (D_2O) τ 0.65 (2 H, m), 1.5 (2 H, m), 4.25 (2 H, s), 5.7 (2 H, q), and 8.8 (3 H, t).

Anal. Calcd for $C_8H_{11}BrN_2O_2$: C, 38.88; H, 4.49; Br, 32.34; N, 11.34. Found: C, 38.78; H, 4.55; Br, 32.48; N, 11.31.

5,6-Dicarbomethoxy-7-carbethoxypyrrolo[1,2-b]pyridazine (12, X = H; R = C_2H_5; R′ = CH_3).—The 1,3-dipolar addition reaction was carried out as for **12** (X = H; R = R′ = CH_3),

(13) R. H. Mizzoni and P. E. Spoerri, *J. Am. Chem. Soc.*, **73**, 1873 (1951).

employing N-(carbethoxymethyl)pyridazinium bromide (3.0 g, 0.012 mole) and dimethyl acetylenedicarboxylate (7.0 g, 0.049 mole) in methylene chloride (50 ml). Dimethyl fumarate was obtained as before and the nonsublimable residue was recrystallized from absolute ethanol yielding buff crystals (1.24 g, 33.4%, mp 133–134°). Repeated recrystallization gave an analytical sample: mp 133.5–134.5°; λ_{max}^{KBr} 5.75, 5.85, and 5.95 μ; nmr ($CDCl_3$) τ 2.82 (3 H, m), 5.54 (2 H, q), 5.97 (3 H, s), 6.06 (3 H, s), and 8.59 (3 H, t).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.81; H, 4.63; N, 9.00.

3,6-Dimethylpyridazine.—This substance was prepared according to the procedure of Overberger, Byrd, and Mesrobian,[14] from 2,5-hexanedione and 85% hydrazine hydrate in 50% yield: bp 95° (12 mm) [lit.[14] 52° (1 mm)], nmr (neat) τ 2.5 (2 H, s) and 7.3 (6 H, s).

N-(Carbomethoxymethyl)-3,6-dimethylpyridazinium Bromide (**11**, **X = R = CH_3**).—The adduct was obtained in the usual way from 3,6-dimethylpyridazine (4.0 g, 0.037 mole) and methyl α-bromoacetate (12.0 g, 0.078 mole) in methylene chloride (50 ml) as pale orange crystals (7.2 g, 75%, mp 155–160°). Recrystallization from methanol–ether provided an analytical sample as buff needles: mp 162–163°; λ_{max}^{KBr} 5.75 μ; nmr (D_2O) τ 2.0 (2 H, s), 4.6 (2 H, s), 6.45 (3 H, s), 7.3 (3 H, s), and 7.45 (3 H, s).

Anal. Calcd for $C_9H_{13}BrN_2O_2$: C, 41.37; H, 5.00; Br, 30.64; N, 10.72. Found: C, 41.09; H, 5.01; Br, 30.60; N, 10.66.

5,6,7-Tricarbomethoxypyrrolo[1,2-*b*]-2-methylpyridazine (**12**, **R = R′ = X = CH_3**).—The 1,3-dipolar addition was carried out as above, using N-(carbomethoxymethyl)-3,6-dimethylpyridazinium bromide (**11**, R = X = CH_3) (5.0 g, 0.017 mole) and dimethyl acetylenedicarboxylate (10.0 g, 0.07 mole) in methylene chloride (150 ml) and a reaction time of 6 hr.

The crude product, a viscous, red residue (17.5 g), was taken up in hot methanol (75 ml), filtered, and allowed to cool slowly. The pale yellow, crystalline product (2.70 g, mp 157–159°) was recrystallized from methanol to provide an analytical sample of white crystals: 2.0 g (25%); mp 164–165° (lit.[9] 164.5–165°); λ_{max}^{KBr} 5.75, 5.85, and 5.95 μ; nmr ($CDCl_3$) τ 2.75 (1 H, s), 3.0 (1 H, s), 6.1 (3 H, s), 6.15 (3 H, s), 6.20 (3 H, s), and 7.4 (3 H, s).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.65; H, 4.61; N, 9.15. Found: C, 54.73; H, 4.67; N, 8.99.

Reaction of N-Carbomethoxyisoquinolinium Bromide with Dimethylacetylene Dicarboxylate. Formation of 1,2-Dihydro-1,2,3-tricarbomethoxy-4,5-benzopyrrocoline (15a) and 1,2,3-Tricarbomethoxy-4,5-benzopyrrocoline (16).—A suspension of N-carbomethoxyisoquinolinium bromide (0.85 g, 3 mmoles), as the above similar adducts from isoquinoline and methyl bromoacetate, in methylene chloride (20 ml), was mixed with dimethyl acetylenedicarboxylate (0.85 g, 6 mmoles) and triethylamine (0.85 g, 8 mmoles), and boiled under reflux for 7 hr. The dark solution was washed with water and saturated aqueous salt, dried over magnesium carbonate, and evaporated to give a red oil. Low-temperature crystallization from methanol afforded a mixture of almost white needles and dark yellow platelets (0.6 g, 60%) which could be separated by placing them on a large filter paper and tapping the edge with a spatula. The heavier platelets marched out to the edge of the paper. Alternatively, careful fractional crystallization from anhydrous methanol effected a satisfactory separation. The nmr spectrum of the mixture showed the peaks later shown to be characteristic of the yellow platelets to be present at twice the intensity of the peaks of the white needles.

The major product (**15a**) was isolated as yellow cubes: mp 142.5–145° after recrystallization from benzene; λ_{max}^{Nujol} 5.73 and 5.95 μ; ultraviolet $\lambda_{max}^{95\%\ C_2H_5OH}$ 253, 305, and 368 mμ (log ϵ 4.30, 3.95, and 4.29); nmr τ ($CDCl_3$) 2.8 (4 H, m), 3.51 (1 H, d, J = 8 cps), 4.15 (1 H, d, J = 8 cps), 4.69 (1 H, d, J = 13 cps), 5.57 (1 H, d, J = 13 cps), 6.02 (3 H, s), 6.12 (3 H, s), and 6.28 (3 H, s).

Anal. Calcd for $C_{18}H_{17}NO_6$: C, 62.97; H, 4.99; N, 4.08; mol wt, 343. Found: C, 63.09; H, 5.18; N, 3.71; mol wt, 343 (parent peak, mass spectrum).

When **15a** was heated at its melting point for 30 min, or boiled in methanol, it was converted in high yield to the second product. This could be isolated as white needles, mp 151.5–152° (lit.[10] 154–155°), by several recrystallizations from methanol: λ_{max}^{Nujol} 5.73, 5.77, and 5.83 μ; ultraviolet $\lambda_{max}^{95\%\ C_2H_5OH}$ 240, 268, 286, 315, 321, 337, and 354 mμ (log ϵ 4.46, 5.40, 4.50, 4.07, 4.03, 4.18, and 4.24); nmr τ ($CDCl_3$) 0.8 (1 H, m), 0.9 (1 H, d, J = 8 cps), 2.6 (3 H, m), 3.01 (1 H, d, J = 8 cps), 6.02 (3 H, s), and 6.09 (6 H, s).

Anal. Calcd for $C_{18}H_{15}NO_6$: C, 63.34; H, 4.43; N, 4.10; mol wt, 341. Found: C, 63.67; H, 4.39; N, 4.08; mol wt, 341 (parent peak, mass spectrum).

Registry No.—**5**, 7593-50-2; benzocinnoline N-oxide, 6141-98-6; **7**, 7593-52-4; **6**, 7202-77-9; benzo[*c*]cinnoline, 230-17-1; **8**, 7593-54-6; **9**, 7593-55-7; **11** (X = H; R = CH_3), 7593-56-8; **11** (X = H; R = Et), 7593-58-0; **11** (X = R = CH_3), 7593-60-4; **12** (X = H; R = R′ = CH_3), 7593-57-9; **12** (X = H; R = Et; R′ = CH_3), 7605-03-0; **12** (R = R′ = X = CH_3), 7593-61-5; 3,6-dimethylpyridazine, 1632-74-2; **15a**, 7593-62-6; **16**, 7593-63-7.

(14) C. G. Overberger, N. R. Byrd, and R. S. Mesrobian, *J. Am. Chem. Soc.*, **78**, 1961 (1956).