Heterodiene Syntheses. Part 20.[1] 4-Arylidene-5-pyrazolones and Ynamines: A [2 + 2]Cycloaddition followed by Electrocyclic Ring Opening, in Competition with a [4 + 2]Cycloaddition; the Influence of the Substituents on the Intermediate

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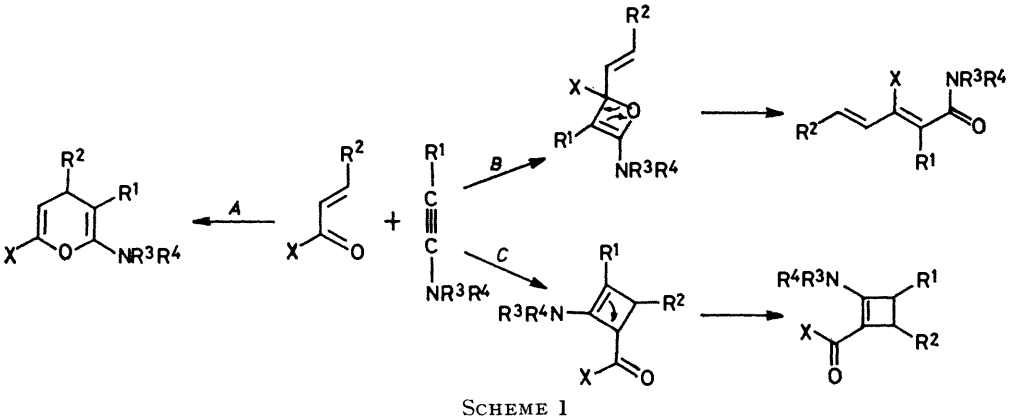
4-Arylidene-5-pyrazolones (1) react with *NN*-diethylaminomethylacetylene to give a mixture of pyrano[2,3-*c*]-pyrazoles (3), in accordance with a [4 + 2]cycloaddition, and 4-(3-aryl-1-diethylamino-2-methylpropenylidene)-pyrazol-5-ones (5) which are formed by electrocyclic ring opening of the [2 + 2]cycloadducts (4). The configuration of the open-chain compounds (5) permits the deduction of that of the originally formed cyclobutene adducts. The reason for the choice between a [4 + 2] and a [2 + 2] cycloaddition can be rationalized in terms of the effect of both the substituents and the configuration of the substrate.

YNAMINES are useful tools in organic synthesis [2] and are particularly versatile reagents in cycloadditions because of the large variety of possible reaction modes. They can react in accordance with a [2 + 2] mode with carbonyl compounds to give oxet derivatives,[3-8] with thiocarbonyl compounds to give thiets,[9] with nitro-derivatives to give oxazets,[10] with the C=C double bond of olefinic [11] and heterocyclic [10] compounds to give cyclobutenes, and with C=N bonds to give azetine derivatives.[12,13] Some of these adducts are stable,[10,11] but in general they are unstable and electrocyclic opening of yields, but become the only product with 9,10-phenanthrenequinone.[18]

If the carbonyl group is part of an ester, a cyclobutene is isolated, which is formed by route *C*, *via* a [2 + 2]-cycloaddition to the C=C bond.[14] These adducts do not give a ring opening but there is double-bond migration to achieve conjugation. With methyl sorbate the addition occurs to the γ,δ C=C bond and the cyclobutene formed gives a δ-dienaminoesters upon ring opening.[19]

This paper reports the reaction of a methyl-substituted ynamine with 4-arylidenepyrazol-5-ones, which have a *Z*-



SCHEME 1

the unsaturated four-membered ring gives open-chain unsaturated compounds.

Since ynamines are nucleophilic reagents, the reactivities of which are controlled by the energy of the highest-occupied molecular orbital, the reaction with $\alpha\beta$-unsaturated carbonyl compounds is very favourable because the reactivity of these electrophilic systems is controlled by the energy of the lowest-unoccupied molecular orbital, and the reaction offers a large variety of possibilities as shown in Scheme 1. If a cisoid conformation can be adopted by the C=C–C=O system, a 1,4-cycloaddition is usually followed,[14-17] *i.e.* route *A*. 1,2-Cycloaddition to the C=O bond (route *B*) gives oxet intermediates [14] which, upon electrocyclic ring opening, form unsaturated amides; these are usually formed in low or *E*-configuration depending on the nature of the substituent in position 3,[20] and whose frontier-orbital energy levels depend on the substituents on the arylidene group.[21]

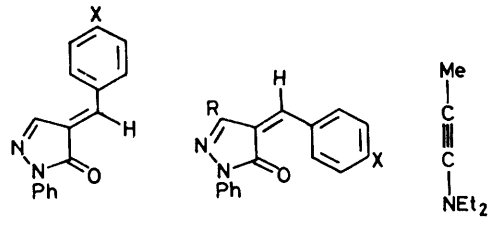
RESULTS AND DISCUSSION

The reaction was performed in cooled benzene (see Experimental section) with the 1-phenyl-4-arylidene-pyrazol-5-ones (1a—m) and *NN*-diethylaminomethyl-acetylene (2).

The reaction gives a mixture of two products, in almost quantitative yield, which can be separated by fractional crystallization and by column chromatography. Both analyse as 1 : 1 adducts.

The colourless adducts had n.m.r. spectra (Table 1) consistent with their formulation as 4-aryl-2-diethyl-

amino-4,7-dihydro-3-methyl-7-phenylpyrano[2,3-*c*]-pyrazoles (3) and they are therefore formed *via* a [4 + 2]cycloaddition.



(2)

E-(1) a; X = NO_2
b; X = Br
c; X = H
d; X = NMe_2

Z-(1) e; R = Me, X = NO_2
f; R = Me, X = Br
g; R = Me, X = H;
h; R = Me, X = NMe_2
i; R = Ph, X = NO_2
j; R = Ph, X = Br
l; R = Ph, X = H
m; R = Ph, X = NMe_2

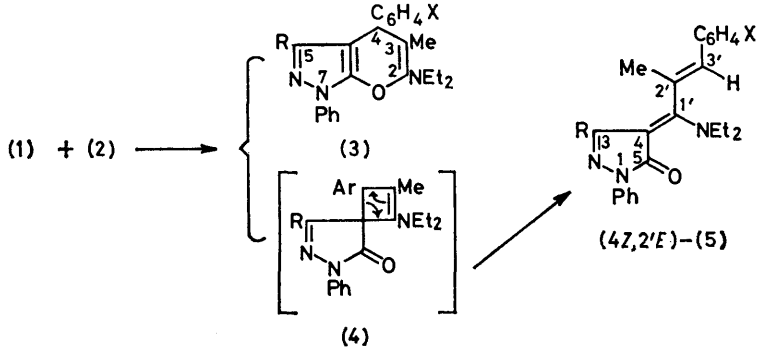
The orange-coloured adducts show a conjugated carbonyl band in the i.r. spectra (ν_{CO}) in the range 1 640—1 650 cm^{-1} depending on the nature of the substituents) and in the n.m.r. spectra (Table 2) there is a signal due to a methyl group which shows allylic coupling to a low-field proton.

established.[22] From these data, the structure of 1-phenyl-4-(1-diethylamino-2-methyl-3-arylpropenylidene)pyrazol-5-one was proposed to be as in (5); this can be formed by a [2 + 2]cycloaddition to the exocyclic C=C double bond, followed by electrocyclic ring opening of the cyclobutene (4) (Scheme 2).

From the n.m.r. data the same configuration can be proposed for all the pyrazolone adducts (5) since the signal of methyl, derived from the ynamine, has an almost identical chemical-shift value [(4a—h), δ 2.20—2.25] independent of the configuration of the starting substrate, and it is only shielded [(4i—m), δ 1.83—1.87] when R = Ph.

These data are inconsistent with (4*E*,2′*E*) and (4*E*,2′*Z*) configurations, since in these configurations the chemical shift of the methyl should be independent of the nature of R. Since the NOE results exclude the (4*Z*,2′*Z*) configuration, the (4*Z*,2′*E*) configuration reported in Scheme 2 can be proposed for (5).

Because of the importance of the configuration of the open-chain adduct in defining the mechanism of the cycloaddition, the deductions from the n.m.r. data were confirmed by *X*-ray analysis of the bromo-substituted adduct (4f) (see Figure and the crystal-structure part of the Experimental Section).



SCHEME 2

The nuclear Overhauser enhancement (NOE) of the methyl signal upon irradiation of the low-field proton is not significant and therefore a *trans* relationship was

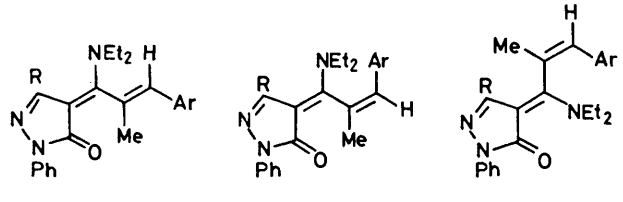
TABLE 1

N.m.r. chemical shifts (δ) for the adducts (3) [Et designated $C(H_B)_3C(H_A)_2$]

Compound	3-Me [a]	4-H [a]	5-R [a]	H_A [b]	H_B [c]	Ar-H	X [a]
(3a)	1.62	4.67	7.18	2.97	1.09	7.2—8.4	
(3b)	1.62	4.54	7.18	2.98	1.10	6.9—8.1	
(3c)	1.62	4.51	*d*	2.94	1.09	7.0—8.0	
(3d)	1.62	4.42	7.21	2.93	1.06	6.6—8.0	2.92
(3e)	1.60	4.57	1.89	2.94	1.07	7.2—8.3	
(3f)	1.60	4.38	1.90	2.93	1.06	7.0—7.9	
(3g)	1.59	4.41	1.88	2.91	1.04	7.2—8.0	
(3h)	1.60	4.29	1.91	2.91	1.06	6.6—8.0	2.90
(3i)	1.66	4.83		2.96	1.07	7.1—8.3	
(3j)	1.65	4.62		2.92	1.03	7.0—8.1	
(3l)	1.64	4.61		2.91	1.02	7.1—7.7	
(3m)	1.67	4.51		2.92	1.02	6.5—8.1	2.89

[a] Singlet. [b] Quartet [coupling constant *J*(AB) always 6.7 Hz]. [c] Triplet. [d] Overlapped by Ar-H.

Where the adducts (5) are stable, the pyran derivatives (3) easily undergo modifications. Heating above the melting point or refluxing in strongly polar solvents causes isomerization to (5). Compounds (3) are also



(4*E*,2′*E*)-(5) (4*E*,2′*Z*)-(5) (4*Z*,2′*Z*)-(5)

unstable both under mild acidic and basic conditions and this lability prevented the use of silica gel during the chromatographic separation of (3) from (5).

The relative yields of (3) and (5) were determined by n.m.r. spectroscopy since the signal of the methyl group

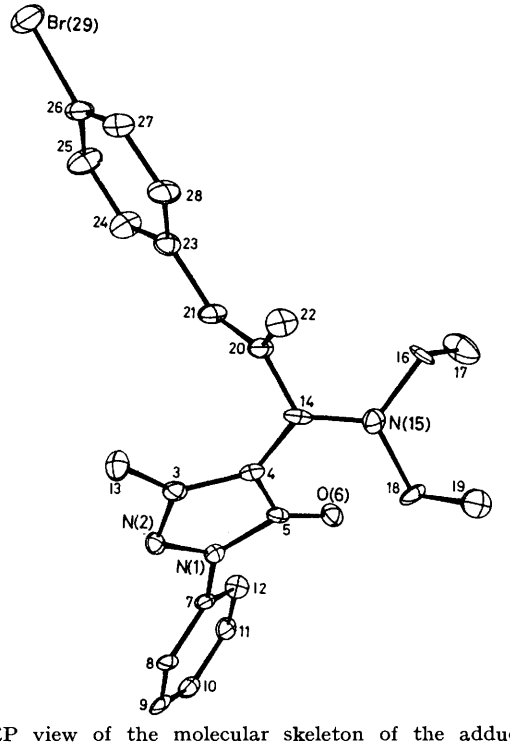
TABLE 2

N.m.r. chemical shifts (δ) for the adducts (5) [Et designated $C(H_B)_3C(H_A)_2$]

Compound	2'-Me [a]	3'-H [b]	3-R [c]	H_A		H_B [d]	Ar-H	X [c]
(5a)	2.20	6.64	*e*	3.55 [f]	4.10 [f]	1.32	7.0—8.4	
(5b)	2.20	6.62	*e*	3.55 [f]	4.10 [f]	1.29	7.1—8.2	
(5c)	2.20	6.67	*e*	3.50 [f]	4.15 [f]	1.28	7.1—8.2	
(5d)	2.20	6.63	*e*	3.51 [b]	4.20 [f]	1.23	6.6—8.3	2.98
(5e)	2.25	6.83	2.09	3.70 [f]		1.28	7.0—8.4	
(5f)	2.20	6.70	2.07	3.70 [f]		1.26	6.9—8.2	
(5g)	2.22	6.78	2.09	3.60 [f]	3.80 [f]	1.26	7.0—8.2	
(5h)	2.23	6.70	2.04	3.53 [b]	3.98 [b]	1.22 1.28	6.7—8.3	3.05
(5i)	1.88	6.66		3.48 [g]	4.12 [g]	1.34	6.8—8.3	
(5j)	1.83	6.65		3.50 [g]	4.10 [g]	1.33 1.35	6.7—8.3	
(5l)	1.87	6.66		3.53 [b]	4.18 [g]	1.33 1.36	6.7—8.4	
(5m)	1.84	6.56		3.49 [g]	4.10 [g]	1.29 1.32	6.4—8.2	2.94

[a] Doublet [coupling constant J(3'H, 2'Me) in the range 1.3—1.5 Hz]. [b] Quartet. [c] Singlet. [d] Triplet [sometimes two signals; coupling constant J(AB) always 6.7 Hz]. [e] Overlapped by Ar-H. [f] Broad band. [g] Broad quartet.

derived from the starting ynamine, is at different positions in each pair of isomers (Tables 1 and 2). The product distributions are given in Table 3; several samples from different preparations gave the same results to within ±2%.



ORTEP view of the molecular skeleton of the adduct (5f) (hydrogen atoms not included); the thermal ellipsoids are depicted according to the output of the last least-squares cycle

The pyrans (3) are the minor products if the pyrazolone has a 3-hydrogen substituent but become the major products if the pyrazolone has a 3-methyl group, irrespective of the substituent X.

This contrasts with the results observed for R = Ph. The lowest yield of (3) occurs when X is the electron-attracting NO_2 group, but its yield increases as the electron-donating character of the X group increases.*

* Further experiments with X = CN and OMe gave 56.3 and 65.0% yields of (3), respectively, which is further support for the trend (all analytical and n.m.r. data are available on request).

These results can be interpreted if compounds (5) are not the primary reaction products but are formed *via* spiro-cyclobutene intermediate (4), if the ring opening of (4) occurs in a conrotatory fashion [23] through the least sterically compressed transition state.[24] Thus the configuration of the spiro-intermediate required to give (5) with a (4*Z*,2'*E*) configuration has the aryl and the pyrazole carbonyl group *trans*.

TABLE 3

Relative yields * of (3) and (5) adducts

Pyrazolone	R	X	(3) (%)	(5) (%)
(1a)	H	NO_2	24.3	75.7
(1b)	H	Br	26.2	73.8
(1c)	H	H	27.5	72.5
(1d)	H	NMe_2	27.9	72.1
(1e)	Me	NO_2	63.5	36.5
(1f)	Me	Br	64.7	35.3
(1g)	Me	H	63.3	36.7
(1h)	Me	NMe_2	62.2	37.8
(1i)	Ph	NO_2	35.3	64.7
(1j)	Ph	Br	58.6	41.4
(1l)	Ph	H	60.3	39.7
(1m)	Ph	NMe_2	69.9	30.1

* The yields are the mean value of 3—5 independent experiments, the methyl region being expanded to a 5 p.p.m. scan width and five integral curves being registered. The error involved is ±2%.

These [2 + 2]cycloadditions could occur through a concerted pathway by using all the 4π electrons of the ynamine triple bond in accordance with a [2 + 2 + 2]-cycloaddition,[25,26] but this would give different cyclobutenes starting from different configurations of (1).

Therefore the formation of the *trans*-cyclobutene starting both from (*E*)- or (*Z*)-pyrazolones (1) can be interpreted if a zwitterionic intermediate is formed, ring closure of which leads to the most favourable configuration of the four-membered adduct (4) (Scheme 3).

The formation of *cis*-cyclobutene is unfavourable because of the interaction arising (empty arrows) between the aryl and the carbonyl group due to the 'down' motion of the former during the ring closure.

However, the opposite motion, needed to give ring closure to the *trans*-(Ar,CO)-cyclobutene (solid arrows), gives rise to interaction between Ar and R. When the group in position 3 of the pyrazole ring offers steric

hindrance (*i.e.* Me not H), the (1,2) cycloaddition is unfavoured.

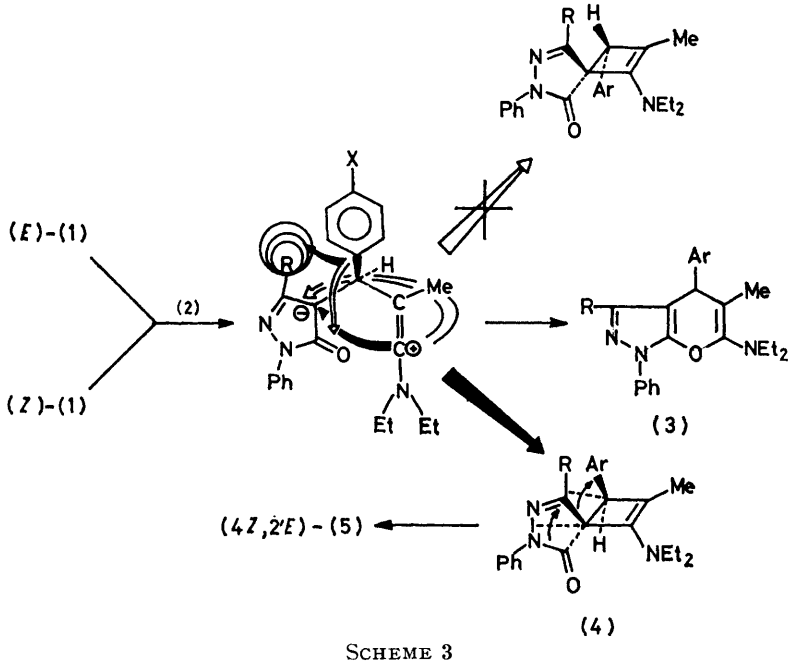
This explanation is correct only if the interaction between Ar and R can be represented in terms of steric repulsion only and therefore the effect of X in the *para* position must be insignificant as observed.

When R = Ph, if X is an electron-attracting group, a favourable dipole–dipole interaction can give anchimeric assistance to the four-membered ring closure. If X is an electron-donating group, the (1,2) cycloaddition is unfavourable. A somewhat similar interaction was found to play a relevant role in the conformation of 2,3-dihydropyrano[2,3-*c*]pyrazoles.[27]

The proposed mechanism assumes the formation of (3) from the same zwitterion which gives rise to (4). Therefore the role of the solvent was investigated since it is well known that zwitterionic intermediates are favoured by polar solvents.[28] Table 4 reports the distribution of adducts for the reaction of (1l) in different solvents.

The yield of the 1,4-cycloadduct (3) increases with both the dielectric constant and the polarity constant (E_T) of the solvent, and if we plot log ([3]/[5]), *i.e.* $\log(k_3/k_5)$, a good linear correlation is obtained, with gradient, intercept, and correlation coefficient of 0.064, −1.978, and 0.989 respectively. This linear dependence between rate and polarity of the solvent can be rationalized only if the zwitterion represented in Scheme 3 is also the intermediate in the cycloaddition which forms (3). Therefore the alternative concerted process, $[4\pi_s + 2\pi_s]$, leading to (3) seems less probable.

The formation of C–C and C–O bonds from the zwitterion can be regarded as arising from the alkylation of an ambident nucleophile (the enolate ion). In non-polar solvents steric interactions are partly counterbalanced by the orbital control involving the two 'soft' carbon centres [29] and the cyclobutenes (4) are the result. In polar aprotic solvents it is known that enolates, in which the carbon atom is relatively hindered, give extensive *O*-alkylation [30] and hence the zwitterion gives ring closure to the pyrans (3). Therefore even if (3) and (5) have the same origin, increasing solvent polarity gives rise to a different distribution of products.



SCHEME 3

TABLE 4

Isomer distribution for the reaction of (1l) and (2) in different solvents

Solvent	ε [a]	E_T [b]	(3l) (%)	(5l) (%)	log (k_3/k_5)
Cyclohexane	2.0	31.2	53.1	46.9	0.05
Benzene	2.3	34.5	60.3	39.7	0.18
Diethyl ether	4.2	34.6	68.3	31.7	0.33
Tetrahydrofuran	7.4	37.4	71.7	28.3	0.40
Acetone	20.7	42.2	83.8	16.2	0.71
Acetonitrile	37.5	46.0	91.3	8.7	1.02

[a] Dielectric constant at 25 °C, values taken from C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, 1968—1969, **11**, 22. [b] Polarity constants at 25 °C, values in kcal mol^{-1} taken from the same reference as in (*a*).

EXPERIMENTAL

I.r. spectra were determined on Nujol mulls with a Perkin-Elmer 257 spectrophotometer. N.m.r. spectra were obtained with a Perkin-Elmer R 12A spectrometer ($CDCl_3$ as solvent) by Dr. A. Gamba Invernizzi. Microanalyses were performed by Dr. L. Maggi Dacrema.

Starting Materials.—1-Phenyl-4-arylidenepyrazol-5-ones (1a—m) were prepared in accordance with the literature method.[20] 1,3-Diphenyl-4-(4-cyanobenzylidene)pyrazol-5-one was prepared in accordance with the previously reported literature method from 1,3-diphenylpyrazol-5-one and *p*-cyanobenzaldehyde as deep red crystals, m.p. 172—173° (ethyl acetate) (Found: C, 78.90; H, 4.45; N, 12.30. $C_{23}H_{15}N_3O$ requires C, 79.07; H, 4.33; N, 12.03%).

Methyl-*NN*-diethylaminoacetylene (2) was redistilled Fluka reagent.

Reaction of Arylidenepyrazol-5-ones (1) *with Ynamine* (2). *General Method.*—A solution of the required pyrazolone (1) (0.005 mol) in benzene (100 ml) was stirred and cooled with ice–water, and ynamine (2) (0.007 mol) dissolved in benzene (5 ml) was added dropwise. Stirring was continued for 20 min at 0 °C and for 2 h at room temperature. After removal of the solvent under vacuum, the deeply coloured viscous oily residue was extracted several times with boiling solvent (see Table 5). The undissolved residue and the coloured material crystallized from the solvent were combined and pure (5) was obtained, after crystallization from ethanol, as deep yellow-to-red crystals. The mother liquors from the extraction were evaporated and the residue was chromatographed on neutral alumina (for elution solvent see Table 5). The first colourless fraction gave pure pyran derivatives (3) as colourless or light cream crystals. Further elution with methanol gave a second crop of (5).

The type of separation and the physical characters of all the adducts (3) and (5) obtained by the above method are reported in Table 5.

N.M.R. Determination of the Relative Yields of (3) *and* (5). *General Method.*—Starting from 0.1 mmol of (1) and following the general method of preparation of (3) and (5) reported above, after removal of the benzene solvent, the reaction mixtures were examined by n.m.r. spectroscopy on an expanded scale (5 p.p.m.), in the region of the formerly ynaminic methyl group (see Tables 1 and 2) for adducts (3) and (5) (a—d) and (i—m). For the adducts (3) and (5) (e—h) the results from this region were further confirmed by those from the region of the pyrazole-methyl group, which gave closely comparable results. As reported in Table 3, the relative yields are the mean value of 3—5 independent experiments, each one being determined with five integral curves. The extreme values were excluded and the variation involved in the best three measurements of each experiment was ±2%. The determination of the relative yields of (3l) and (5l) in different solvents (Table 4) was performed under identical experimental conditions, using identical volumes of the required solvent.

Isomerization of (3g) *to* (5g).*—(*a*) A solution of (3g) (0.075 g, 0.2 mmol) in freshly distilled anhydrous acetonitrile (1.0 ml) was heated at 85 °C in a sealed tube for 48 h. The brown-orange solution was evaporated to dryness and the oily residue was treated with a small volume of diethyl ether. Cooling gave 0.045 g (60% yield) of orange crystals identical

TABLE 5

Preparation and analytical data of adducts (3) and (5)

Compound	Type of separation [a]	M.p. (°C) (solvent)	Elemental analyses (%)		
(3a)	A	75—76 [b]	Found:		C, 67.9; H, 6.0; N, 14.1
(5a)	B	139—140 [c]	Found:		C, 67.95; H, 6.1; N, 14.05
			$C_{23}H_{24}N_4O_3$	requires	C, 68.3; H, 6.0; N, 13.85
(3b)	C	73—74 [d]	Found:		C, 62.8; H, 5.55; N, 9.65
(5b)	B	125—126 [c]	Found:		C, 62.7; H, 5.65; N, 9.55
			$C_{23}H_{24}N_3OBr$	requires	C, 63.0; H, 5.5; N, 9.6
(3c)	C	127—128 [e]	Found:		C, 76.7, H, 7.15, N, 11.7
(5c)	D	102—103 [c]	Found:		C, 76.7; H, 7.0; N, 11.6
			$C_{23}H_{25}N_3O$	requires	C, 76.85; H, 7.0; N, 11.7
(3d)	E	85—86 [e]	Found:		C, 74.25; H, 7.85; N, 14.1
(5d)	F	109—110 [c]	Found:		C, 74.2; H, 7.6; N, 13.85
			$C_{25}H_{30}N_4O$	requires	C, 74.6; H, 7.5; N, 13.9
(3e)	C	114 [e]	Found:		C, 68.9; H, 6.3; N, 13.4
(5e)	F	156 [c]	Found:		C, 68.55; H, 6.3; N, 13.25
			$C_{24}H_{26}N_4O_3$	requires	C, 68.9; H, 6.3; N, 13.4
(3f)	C	85—86 [e]	Found:		C, 63.8; H, 5.7; N, 9.4
(5f)	F	135—136 [c]	Found:		C, 63.55; H, 5.65; N, 9.55
			$C_{24}H_{25}N_3OBr$	requires	C, 63.7; H, 5.75; N, 9.3
(3g)	C	84 [e]	Found:		C, 76.8; H, 7.3; N, 11.45
(5g)	D	149—150 [c]	Found:		C, 77.15; H, 7.55; N, 11.15
			$C_{24}H_{27}N_3O$	requires	C, 77.2; H, 7.3; N, 11.25
(3h)	C	104 [e]	Found:		C, 74.7; H, 7.95; N, 13.4
(5h)	D	186 [c]	Found:		C, 74.7; H, 7.85; N, 13.35
			$C_{26}H_{32}N_4O$	requires	C, 75.0; H, 7.75; N, 13.45
(3i)	E	128—129 [e]	Found:		C, 72.25; H, 6.0; N, 11.55
(5i)	B	185—186 [c]	Found:		C, 72.05; H, 5.85; N, 11.45
			$C_{29}H_{28}N_4O_3$	requires	C, 72.5; H, 5.85; N, 11.65
(3j)	C	114—115 [e]	Found:		C, 68.05; H, 5.7; N, 8.25
(5j)	B	148—149 [c]	Found:		C, 67.95; H, 5.85; N, 8.4
			$C_{29}H_{28}N_3OBr$	requires	C, 67.7; H, 5.45; N, 8.15
(3l)	C	200—201 [e]	Found:		C, 80.1; H, 6.9; N, 9.55
(5l)	B	160—161 [c]	Found:		C, 79.8; H, 6.75; N, 9.55
			$C_{29}H_{29}N_3O$	requires	C, 79.95; H, 6.7; N, 9.65
(3m)	E	175—176 [b]	Found:		C, 77.5; H, 7.3; N, 12.0
(5m)	B	179—180 [c]	Found:		C, 77.85; H, 7.2; N, 11.9
			$C_{31}H_{34}N_4O$	requires	C, 77.8; H, 7.15; N, 11.7

[a] A: chromatographic separation with cyclohexane–ethyl acetate (8 : 2) as eluant; B: residue after extraction of the reaction mixture with boiling cyclohexane; C: chromatographic separation with cyclohexane as eluant; D: residue after extraction of the reaction mixture with boiling light petroleum (b.p. 30—50 °C); E: chromatographic separation with cyclohexane–ethyl acetate (9 : 1) as eluant; F: residue after extraction of the reaction mixture with boiling light petroleum (b.p. 60—80 °C). [b] Cyclohexane. [c] Ethanol. [d] Light petroleum (b.p. 30—50 °C). [e] Light petroleum (b.p. 60—80 °C).

* Comparable conditions allow the isomerization of each adduct (3).

TABLE 6

Bond lengths (Å; estimated standard deviation <0.01 Å) and bond angles (°; estimated standard deviation <1°); figures involving hydrogen atoms are not listed

(*a*) Bond lengths

N(1)–N(2)	1.37	N(15)–C(16)	1.46
N(2)–C(3)	1.33	N(15)–C(18)	1.49
C(3)–C(4)	1.44	C(16)–C(17)	1.48
C(4)–C(5)	1.47	C(18)–C(19)	1.52
N(1)–C(5)	1.40	C(14)–C(20)	1.49
C(5)–O(6)	1.23	C(20)–C(21)	1.34
N(1)–C(7)	1.43	C(20)–C(22)	1.53
C(7)–C(8)	1.38	C(21)–C(23)	1.48
C(7)–C(12)	1.39	C(23)–C(24)	1.38
C(8)–C(9)	1.46	C(23)–C(28)	1.36
C(9)–C(10)	1.36	C(24)–C(25)	1.39
C(10)–C(11)	1.37	C(25)–C(26)	1.33
C(11)–C(12)	1.40	C(26)–C(27)	1.36
C(3)–C(13)	1.49	C(27)–C(28)	1.39
C(4)–C(14)	1.43	C(36)–Br(29)	1.88
C(14)–N(15)	1.35		

(*b*) Bond angles

N(1)–N(2)–C(3)	108	C(14)–N(15)–C(16)	122
N(2)–N(1)–C(5)	114	C(14)–N(15)–C(18)	121
N(2)–C(3)–C(4)	108	C(16)–N(15)–C(18)	116
C(3)–C(4)–C(5)	109	N(15)–C(16)–C(17)	114
C(4)–C(5)–N(1)	106	N(15)–C(18)–C(19)	112
C(4)–C(5)–O(6)	133	C(4)–C(14)–C(20)	120
N(1)–C(5)–O(6)	126	N(15)–C(14)–C(20)	116
N(2)–N(1)–C(7)	119	C(14)–C(20)–C(21)	116
C(5)–N(1)–C(7)	126	C(14)–C(20)–C(22)	118
N(1)–C(7)–C(8)	119	C(22)–C(20)–C(21)	126
N(1)–C(7)–C(12)	121	C(20)–C(21)–C(23)	131
C(8)–C(7)–C(12)	121	C(21)–C(23)–C(24)	117
C(7)–C(8)–C(9)	117	C(21)–C(23)–C(28)	128
C(8)–C(9)–C(10)	121	C(23)–C(24)–C(25)	122
C(9)–C(10)–C(11)	120	C(24)–C(25)–C(26)	121
C(10)–C(11)–C(12)	120	C(25)–C(26)–C(27)	119
C(7)–C(12)–C(11)	121	C(26)–C(27)–C(28)	120
N(2)–C(3)–C(13)	120	C(27)–C(28)–C(23)	123
C(4)–C(3)–C(13)	132	C(28)–C(23)–C(24)	115
C(3)–C(4)–C(14)	128	C(25)–C(26)–Br(29)	121
C(5)–C(4)–C(14)	123	C(27)–C(26)–Br(29)	120
C(4)–C(14)–C(15)	123		

in every respect with a sample of (5g). A second crop of (5g) (about a further 20%) was obtained by column chromatography on neutral alumina.

(*b*) Compound (3g) (0.2 mmol) was heated in a sealed tube at 120 °C for 14 h. The oily residue was treated as above and yielded (5g) (*ca.* 80%).

X-*Ray Analysis*.—*Crystal data*. (5f); $C_{24}H_{26}N_3OBr$, orange-red crystals, space group $P2_1/c$, $a = 17.956(6)$, $b = 10.320(2)$, $c = 12.422(2)$ Å, $\beta = 104.922°(9)$, $Z = 4$. The crystal used had dimensions 0.48 × 0.42 × 0.03 mm. Intensity data were collected on a Philips PW 1100 computer-controlled four-circle diffractometer using the ω—2θ scan technique, graphite-monochromatized Cu-K_α radiation, $\lambda = 1.5418$ Å, $\theta_{max.} = 50°$.

TABLE 7

Significant torsion angles (°) (estimated standard deviation in the range 0.7—1.0°)

N(2)–N(1)–C(7)–C(8)	142.0
N(2)–N(1)–C(7)–C(12)	−37.1
C(3)–C(4)–C(14)–C(20)	151.5
C(5)–C(4)–C(14)–C(20)	−33.0
C(3)–C(4)–C(14)–N(15)	−28.9
C(5)–C(4)–C(14)–N(15)	146.5
C(14)–N(15)–C(18)–C(19)	46.4
C(16)–N(15)–C(18)–C(19)	−128.3
C(17)–C(16)–N(15)–C(18)	−113.8
C(14)–N(15)–C(16)–C(17)	71.5
C(4)–C(14)–N(15)–C(18)	155.2
C(4)–C(14)–N(15)–C(16)	30.4
C(20)–C(14)–N(15)–C(18)	−25.3
C(20)–C(14)–N(15)–C(16)	149.1
C(20)–C(21)–C(23)–C(24)	−0.9

The 3 300 independent reflections were processed according to the method of Davies and Gatehouse [31] to yield values of F_o and $\sigma(F_o)$, the 2 164 reflections with $I > 2\sigma(I)$ being regarded as observed. The co-ordinates of the heavy atom were obtained from a three-dimensional Patterson synthesis. A subsequent electron-density map computed with the phases given by the heavy atom revealed all the remaining non-hydrogen atoms. The structure was refined anisotropically with the program ORFLS,[32] the final R' being 0.093 for the observed reflections. Scattering factors for neutral atoms were those of Doyle and Turner [33] and for the hydrogen atoms those of Stewart *et al.*[34]

Bond lengths and angles not involving hydrogen atoms are listed in Table 6, the more significant torsion angles are given in Table 7, and an analysis of the planarity of the rings and conjugated systems is provided in Table 8. Tables of structure factors, atomic fractional co-ordinates, and thermal parameters are listed in Supplementary Publication No. SUP 22366 (24 pp.).*

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TABLE 8

Distances (Å) of atoms from their least-squares planes; each plane comprises all the atoms whose distances from it are listed (estimated standard deviations <0.01 Å). Atom numbering as in Figure 1

Pyrazolone ring	N(1)	N(2)	C(3)	C(4)	C(5)	O(6)	C(13)	C(14)
	−0.015	+0.019	−0.018	+0.023	+0.038	−0.015	−0.023	−0.032
N-Phenyl ring	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)		
	−0.016	+0.013	−0.004	−0.002	−0.004	+0.015		
Double-bond plane	C(14)	C(20)	C(21)	C(22)	C(23)			
	+0.003	−0.002	−0.006	−0.087	+0.005			
Br-phenyl ring	C(23)	C(24)	C(25)	C(26)	C(27)	C(28)	Br(29)	
	+0.045	−0.004	−0.025	−0.054	−0.032	+0.008	+0.001	

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