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HETERODIENE SYNTHESES—XIX[1]

CORRELATION OF THE KINETIC DATA WITH LUMO ENERGIES IN THE REACTION BETWEEN 1-ARYL-4-BENZYLIDENE-5-PYRAZOLONES AND ISOPROPYL VINYL ETHER

G. Desimoni,* P. P. Righetti, E. Selva and G. Tacconi
Istituto di Chimica Organica dell'Università, 27100 Pavia, Italy

and

V. Riganti and M. Specchiarello
Istituto di Chimica Generale e Inorganica dell'università, 27100, Pavia, Italy

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Abstract—The kinetics of the reaction between 1-*p*-substituted phenyl-4-benzylidene-5-pyrazolones and isopropyl vinyl ether have been studied by quantitative spectroscopic analysis and liquid chromatography. The rate increases with the electron attracting character of the substituents and a correlation is obtained with σ constants. The polarographic one-electron half-wave reduction potentials $E^{red}_{1/2}$, which represent an experimental measure for the relative energy of the lowest unoccupied molecular orbital (LUMO), were measured. Good correlations were obtained between these and the kinetic data, thus demonstrating the frontier-controlled character of the cycloaddition and the dominant interaction between the LUMO of the pyrazolone and the highest occupied molecular orbital (HOMO) of the vinyl ether.

In previous papers[1,2] we have investigated the effect of substituents on the kinetic data of the 1,4-cycloaddition between 4-arylidene-5-pyrazolones and alkyl vinyl ethers.

Whereas the substituent in position 3 alone has no effect[1] on the rate, the substituent on the 4-arylidene group, which is directly conjugated with the C=C–C=O system, has a strong influence[2] and the rate increases with an electron withdrawing group.

In this paper we wish to report the results of the investigation into the effect of substituents in the *para* position of the 1-phenyl group since cross-conjugation, via the pyrazole nitrogen lone pair, can occur between this and the α,β-unsaturated carbonyl system. This is shown by the variation of the double bond orders in some model compounds.[3]

RESULTS

The tedious preparation of the starting materials follows that of the unsubstituted 1-phenyl-4-benzal-5-pyrazolone[4] but starting from suitably substituted phenylhydrazines (Scheme 1). Hydrazones **1a–e** were cyclized **2a–e**, hydrolyzed and decarboxylated† and, without isolating, directly condensed with benzaldehyde. 1-Aryl-4-benzylidene-5-pyrazolones **3a–e** prepared in this way have an **E** configuration since their NMR spectra show no signal at about 8.5 δ which would occur with arylidene protons deshielded by the carbonyl group.[5]

The reaction of these with isopropyl vinyl ether gave a mixture of *cis*- and *trans*-2-isopropoxy-4-phenyl-7-aryl-2,3-dihydropyran[2,3-c]pyrazoles **4** and **5a–e**.

The kinetic runs were performed in benzene at 70° and followed to 60–80% completion by quantitative spectroscopic analysis of the disappearing pyrazolones **3** (experimental). The reactions between pyrazolones and vinyl ethers are second-order, first-order with respect to each reagent,[2] and preliminary experiments performed in **3b** confirmed this to be true in this case too.

A 200-fold molar excess of vinyl ether gave pseudo-first-order conditions and the overall rate constants k_{tot} were measured in this way. The molar ratio $\alpha = [cis$ adduct$]/[trans$ adduct$]$ was previously determined by TLC and UV spectroscopic analysis,[2] but a liquid chromatograph with a UV-Vis Beckman mod. 25 spectrophotometer as detector was made available in our Institute. Using a calibration curve (Experimental for details) better α values were obtained which, compared with α values determined by TLC, showed the latter technique oversetimated the lower yield isomer (Table 1). For this reason the unsubstituted 1-phenyl-4-benzal-5-pyrazolone **4f** was remonitored and the α value, previously determined as 2.38 (**4f**:**5f** = 70.5:29.2),[2] was found to be 3.44 (**4f**:**5f** = 77.5:22.5) by the liquid chromatography.

The rate constants were determined from $k_{tot} = k_{cis} + k_{trans}$ and $\alpha = k_{cis} : k_{trans}$ and the results are shown in Table 1.

Both log k_{cis} and log k_{trans} gave Hammett-type relationships, analogous to those of 1-phenyl-4-p.aryliden-substituted-5-pyrazolones,[2] but a better correlation occurs if σ constants[6] are plotted instead of $\sigma +$.ρ values are quite similar: 0.568 for k_{cis} and 0.612 for k_{trans} with correlation coefficients of 0.990 and 0.980 respectively.

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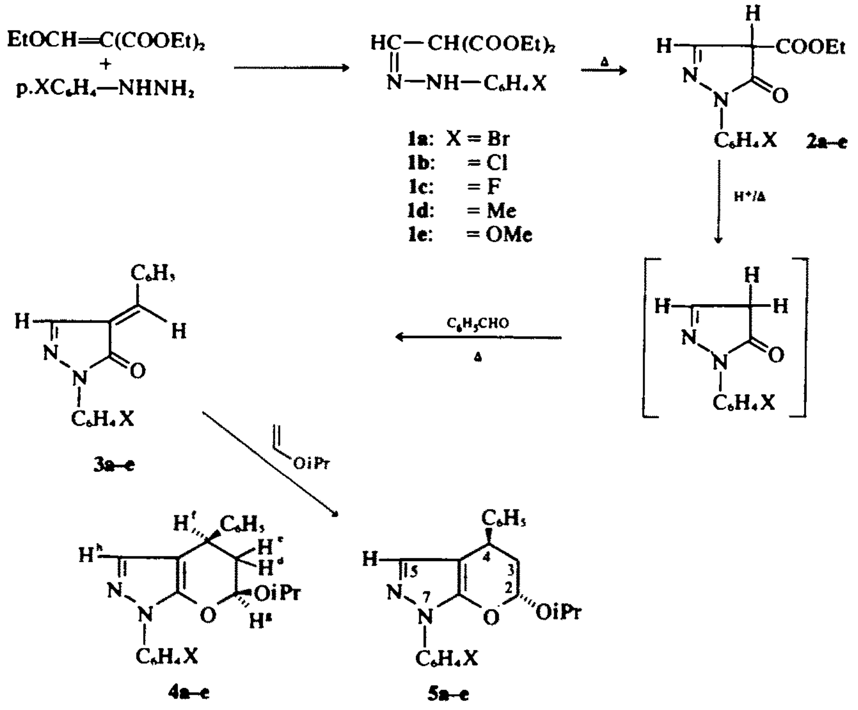
†*p*-Nitrophenyl-hydrazone (m.p. 143.5°) and 1-*p*-nitrophenyl-4-carbomethoxy-5-pyrazolone (m.p. 201°) were also easily obtained, but every attempt to hydrolyze and decarboxylate the latter was unsucccesful.



Scheme 1.

Table 1. Rate constants (l mol^{-1} s^{-1}) for the reaction of 1-aryl-4-benzylidene-5-pyrazolones (**3a–f**) with isopropyl vinyl ether at 70° in benzene

Pyrazolone	$10^4\ k_{tot}$	TLC + UV		Liq.chrom.		$10^4\ k_{cis}$	$10^4\ k_{trans}$
		% 5	α	% 5	α		
3a	16.0 ± 0.5	71.5	2.51	79	3.76	12.6	3.36
3b	14.3 ± 0.6	68.5	2.17	79.5	3.88	11.4	2.93
3c	11.9 ± 0.5	71.5	2.51	78	3.55	9.28	2.62
3d	8.96± 0.2	69	2.23	79	3.76	7.08	1.88
3e	7.74± 0.05	69	2.23	80.5	4.13	6.23	1.51
3f	10.9[a]	70.5[a]	2.38[a]	77.5	3.44	8.45[b]	2.45[b]

[a] Value taken from ref.2. [b] In ref.2 reported as k_{cis} 7.67 and k_{trans} 3.23.

Rationalization of the kinetic data variation in terms of common dipolar intermediate giving rise to 4 and 5 although the α value is nearly independent of variation in the substituent, cannot be accepted, because the low yield *trans* adducts 5 are thermodynamically more stable than the *cis* ones 4. A better rationalization in terms of the $\mathrm{HOMO_{vinylether}/LUMO_{pyrazolone}}$ interaction[7] can be accepted if one assumes the constant σ represents the effect of the group on the energy level of the LUMO of 3.

It is well known[8] that the energy of the LUMO (E_{LUMO}) of an electron-acceptor molecule is equal to the negativity of the electron affinity (EA). There is a relationship (eqn 1) between EA and the polarographic one-electron half-wave reduction potential ($E_{1/2}^{red}$) which allows this technique to be used as an effective method of measuring the variation of E_{LUMO} on a given series if the differences between the solvation energy of the anion and the neutral acceptor molecule (ΔF_{solv}) is a constant.

$$E_{LUMO} = -EA + E_{1/2}^{red} - \Delta F_{solv} - \mathrm{Constant} \quad (1)$$

The $E_{1/2}^{red}$ values for **3a–e** were measured (see experimental for details) and were plotted in Fig. 1 against log k. Good correlations were obtained (slopes and correlation coefficients: −3.997, 0.989 for log k_{cis} and −4.361, 0.991 for log k_{trans}) which clearly indicate the

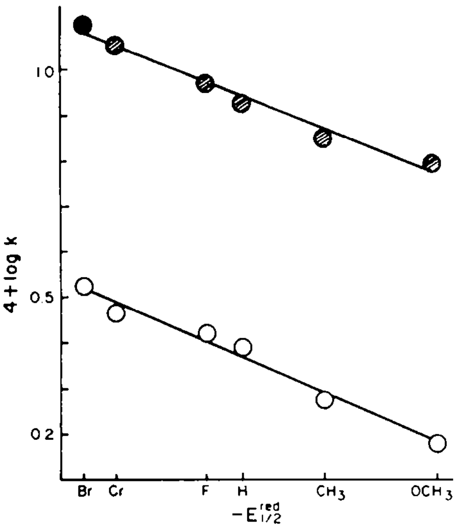


Fig. 1. Correlation of log k_{cis} (▨) and log k_{trans} (○) and $-E^{red}_{1/2}$ for the reaction of 1-aryl-4-benzylidene-5-pyrazolones and isopropyl vinyl ether in benzene at 70°.

frontier-controlled character of the reaction between aryliden-pyrazolones and vinyl ethers and the dependence of the kinetic data on the energy of the LUMO of the pyrazolone if the vinyl ether is taken as a constant.

Furthermore the physical meaning of the various Hammett-type relationships with the kinetic data[1,2] can only be understood if the substituent constants do not express the influence of the substituent on the rest of the molecule or on the cycloaddition transition state, but are simply taken as a measure of the variation of the energies of the frontier molecular orbitals. If the polarographic reduction potentials are taken to represent E_{LUMO}, the series must be homogeneous so that ΔF_{solv} in eqn (1) can be taken as a constant. If this is so, we believe that an easy and valuable estimation of the relative value of E_{LUMO} can be obtained as well as E_{HOMO} values taken from ionization potentials.

This allows complete experimental representation of HOMO and LUMO orbitals, which will be very useful in studying all the reactions which are under frontier control.

EXPERIMENTAL

IR spectra (Nujol mulls) were obtained with a Perkin Elmer 257 spectrophotometer. NMR data were obtained by Dr. Anna Gamba Invernizzi with a Perkin Elmer R 12 A spectrometer (solvent $CDCl_3$, TMS as internal standard). M.ps are uncorrected.

Dicarboxyethylacetaldehyde p-*substituted phenylhydrazone* (1a–e)

General procedure. p-Substituted phenylhydrazine hydrochloride (0.02 M) was dissolved in the minimum amount of cold water and 50% KOHaq (20 ml) was added. The free base ppt was filtered off, dried and dissolved in the minimum amount of EtOH. Ethoxymethylenemalonate (0.022 M) was added and the soln was refluxed for 40′. Solvent was distilled off and the red oil residue was crystallized from diisopropyl ether. All compounds are reported in Table 2.

1-p-*Substituted phenyl-4-carboxyethyl-5-pyrazolones* (2a–e)

General procedure. A sample of **1** (0.015 M) was heated in a test tube over an oil bath at 160–165° (120–125° for **1e**) for 40′. EtOH (about 5 ml) was carefull added to the melted mixture and cooling gave **2**, whose properties are reported in Table 3.

1-p-*Substituted phenyl-4-benzal-5-pyrazolones* (3a–e)

General procedure. A mixture of **2** (0.01 M) and 20% NaOHaq (120 ml) was heated over an oil bath at 115–120° (100–105° for **2d**) for 60 hr. The yellow soln was filtered and acidified with conc. HCl. After cessation of CO_2 evolution, the mixture was further heated 4 hr at 115–120° (**2d** at 100–105°) under N_2. The solid was filtered and extracted with benzene in soxhlet and the mother liquors were extracted with diethylether. 1-*p*-Substituted phenyl-5-pyrazolones were not isolated but their solns, extracted from the solid and the mother liquors, were evaporated and the residue condensed with a slight excess of benzaldehyde by warming at 140–145° for 45 min. The mixtures, after cooling, were crystallized from EtOH and 1-*p*-substituted-3 separated as coloured solids, whose characteristics are given in Table 4.

cis[2, 4] *and* trans[2, 4] *2-Isopropoxy-4-phenyl-7-aryl-2,3-dihydropyrano* [2,3-c] *pyrazoles* (4 *and* 5a–e)

General procedure Pure isomers were prepared from the appropriate pyrazolone (**3**) (0.001 M) and isopropyl vinyl ether[9] (0.03 M) at 70° until the orange colour of the pyrazolone disappeared, as described in part XV of this series.[2] Type of separation, characters and elemental analyses are reported in

Table 2. Properties of hydrazones 1

Compd	m.p. (°C) (Yield %)	Elementary analysis		IR (ν/cm^{-1}) (ν_{NH})
1a; X = Br	117.5 (63)	for $C_{14}H_{17}N_2O_4Br$	found: C, 46.80; H, 4.79; N, 7.82 calc: C, 47.07; H, 4.80; N, 7.84%	3300
1b; = Cl	116 (38)	for $C_{14}H_{17}N_2O_4Cl$	found: C, 53.99; H, 5.50; N, 8.97 calc: C, 53.76; H, 5.48; N, 8.96%	3300
1c; = F	113 (30)	for $C_{14}H_{17}N_2O_4F$	found: C, 56.67; H, 5.83; N, 9.31 calc: C, 56.75; H, 5.78; N, 9.46%	3300
1d; = Me	85.5 (42.5)	for $C_{15}H_{20}N_2O_4$	found: C, 61.67; H, 6.97; N, 9.66 calc : C, 61.63; H, 6.90; N, 9.58%	3300
1e; = OMe	62 (40)	for $C_{15}H_{20}N_2O_5$	found: C, 58.59; H, 6.43; N, 9.22 calc: C, 58.43; H, 6.54; N, 9.09%	3310

Table 3. Properties of 4-carboxyethyl-5-pyrazolones **2**

Compd	Yield %[a]	m.p. (°C) (solvent)		Elementary analysis
2a	66	154		found: C, 45.98; H, 3.57; N, 9.02
		(MeOH)	for $C_{12}H_{11}N_2O_3Br$	calc: C, 46.32; H, 3.56; N, 9.00%
2b	68	149		found: C, 53.80; H, 4.23; N, 10.65
		(MeOH)	for $C_{12}H_{11}N_2O_3Cl$	calc: C, 54.04; H, 4.16; N, 10.50%
2c	79	142		found: C, 57.41; H, 4.58; N, 11.46
		(MeOH)	for $C_{12}H_{11}N_2O_3F$	calc: C, 57.60; H, 4.43; N, 11.20%
2d	57	128		found: C, 63.49; H, 5.81; N, 11.05
		(MeOH)	for $C_{13}H_{14}N_2O_3$	calc: C, 63.40; H, 5.73; N, 11.38%
2e	51	131		found: C, 59.35; H, 5.54; N, 10.74
		(MeOH)	for $C_{13}H_{14}N_2O_4$	calc: C, 59.53; H, 5.38; N, 10.68%

[a] Given on the crystallized matherial.

Table 4. Properties of 1-aryl-4-benzal-5-pyrazolones **3**

Compd	Yield %[a]	m.p. (°C) (solvent)		Elementary analysis
3a	17	189		found: C, 58.60; H, 3.57; N, 8.71
		(EtOH)	for $C_{16}H_{11}N_2OBr$	calc: C, 58.74; H, 3.39; N, 8.56%
3b	23	180		found: C, 67.61; H, 3.99; N, 9.97
		(EtOH)	for $C_{16}H_{11}N_2OCl$	calc: C, 67.97; H, 3.92; N, 9.91%
3c	35	177		found: C, 71.94; H, 4.29; N, 10.26
		(EtOH)	for $C_{16}H_{11}N_2OF$	calc: C, 72.17; H, 4.16; N, 10.52%
3d	25	193		found: C, 77.72; H, 5.43; N, 10.47
		(EtOH)	for $C_{17}H_{14}N_2O$	calc: C, 77.84; H, 5.38; N, 10.68%
3e	19	156		found: C, 73.27; H, 5.36; N, 10.13
		(EtOH)	for $C_{17}H_{14}N_2O_2$	calc: C, 73.36; H, 5.07; N, 10.07%

[a] Given on the crystallized matherial.

Table 5. The configuration of each adduct was assigned by NMR whose parameters, from a simple analysis of the spectra, are reported in Table 6.

Kinetic determinations The overall reaction rates were measured by following the disappearance of **3** at 330 nm on a Beckman DU-2 spectrophotometer, in accordance with the method previously described.[2] Some preliminary experiments (Table 7) gave results fitting the second order rate eqn (2) with C_{VE} and C_P, the initial concentrations of the vinyl ether and the pyrazolone respectively, and $g = (A_0 - A_t)/A_0$ with A_0 and A_t the absorbance of the pyrazolone at times zero and t respectively.

$$K_2 t = \frac{1}{C_{VE} - C_P} \ln \frac{C_P (C_{VE} - C_P g)}{C_{VE} (C_P - C_P g)} \tag{2}$$

Using a large initial concentration of vinyl ether and a low concentration of pyrazolone the results fit a first-order eqn (3) with both rate constants in good agreement (Table 7). Therefore, under these conditions, pseudo-first-order rate constants were determined (Table 1).

$$K_{tot} t = \frac{1}{C_{VE} - C_P} \ln (A_0/A_y). \tag{3}$$

Table 5. Properties of 2-isopropoxy-4-phenyl-7-p-substitutedphenyl-2,3-dihydrpyrano [2,3-c] pyrazoles **4** and **5**

Compd	Type of separation[a]	m.p. (°C)	(solvent)		Elementary analysis
4a	B	109	(EtOH)		found: C, 60.91; H, 5.01; N, 6.90
5a	B + A	120	(Petrol ether)		found: C, 60.77; H, 5.38; N, 7.03
				for $C_{21}H_{21}N_2O_2Br$	calc: C, 61.02; H, 5.12; N, 6.78%
4b	B	106	(EtOH)		found: C, 68.21; H, 5.47; N, 7.71
5b	B + A	116	(Petrol ether)		found: C, 68.49; H, 5.48; N, 7.49
				for $C_{21}H_{21}N_2O_2Cl$	calc: C, 68.38; H, 5.74; N, 7.60%
4c	B	83	(EtOH)		found: C, 71.39; H, 5.98; N, 8.13
5c	B + A	128	(Petrol ether)		found: C, 71.61; H, 5.94; N, 8.23
				for $C_{21}H_{21}N_2O_2F$	calc: C, 71.57; H, 6.01; N, 7.95%
4d	A	89	(MeOH)		found: C, 76.04; H, 7.00; N, 7.91
5d	A	114	(Petrol ether)		found: C, 75.95; H, 7.21; N, 7.88
				for $C_{22}H_{24}N_2O_2$	calc: C, 75.83; H, 6.94; N, 8.04%
4e	A	109	(EtOH)		found: C, 72.77; H, 6.31; N, 7.73
5e	A	107	(Petrol ether)		found: C, 72.38; H, 6.80; N, 7.88
				for $C_{22}H_{24}N_2O_3$	calc: C, 72.50; H, 6.64; N, 7.69%

[a] **A**: chromatographic separation on silicagel H Merck with cyclohexane/ethyl acetate 9:1 as eluant; **B**: fractional crystallization from EtOH.

Table 6. NMR spectra of adducts **4** and **5** (iPr designated $CH_a \circ C(H_b)_3C(H_c)_3$; for H_{d-h} see formula 4 in Scheme 1)

Compd	Chemical shifts (δ)										Coupling constants (Hz)					
	H_d	H_e	H_f	H_g	H_h	H_a	H_b	H_c	Ar–H	HX	J_{ab}	J_{dg}	J_{eg}	J_{df}	J_{ef}	$-J_{de}$
4a	2.11	2.36	4.10	5.51	a	4.1	1.21	1.31	7.1–7.95	–	5.3	6.8	2.9	8.4	6.9	13.3
4b	2.14	2.41	4.13	5.56	a	4.05	1.22	1.34	7.2–8.0	–	6.0	7.3	3.0	8.2	6.7	13.9
4c	2.10	2.30	4.16	5.49	a	4.15	1.12	1.30	6.9–7.95	–	5.3	7.6	2.9	8.9	6.5	13.8
4d	2.11	2.35	4.11	5.46	a	4.1	1.13	1.33	7.1–7.8	2.36	5.7	7.1	3.1	9.0	6.2	13.4
4e	2.08	2.32	4.10	5.48	a	4.0	1.15	1.28	6.9 7.85	3.80	5.3	7.6	3.0	7.6	5.4	13.3
5a	1.92	2.20	4.17	5.60	7.20	4.05	1.12	1.22	7.2 7.9	–	6.2	2.5	2.4	11.1	5.9	13.8
5b	1.85	2.21	4.16	5.59	a	4.0	1.13	1.23	7.0 7.9	–	6.2	2.5	2.4	11.0	5.8	13.8
5c	1.89	2.20	4.16	5.56	a	4.05	1.12	1.23	7.0 7.9	–	6.2	2.5	2.4	11.1	5.8	13.8
5d	1.90	2.21	4.18	5.55	7.18	4.05	1.13	1.22	7.2 8.0	2.36	6.2	2.5	2.4	11.2	5.9	13.8
5e	1.88	2.18	4.17	5.58	7.18	4.0	1.13	1.23	7.2 8.0	3.80	6.2	2.5	2.4	11.2	5.9	13.8

Table 7. Overall rate constants for reactions of 1-p.chlorophenyl-4-benzal-5-pyrazolone (**3b**; initial concn = C_p) with isopropyl vinyl ether. (initial concn = C_{ve}) at 70° in benzene

Run	$10^3\ C_p$	$10^3\ C_{ve}$	C_{ve}/C_p	$10^3\ k_{tot}$
1[a]	1.14	16.44	14.42	1.28 [b]
2[a]	1.15	20.83	18.11	1.25 [b]
3	0.62	48.04	77.48	1.34 [c]
4	0.71	104.94	147.80	1.47 [c]
5	0.77	226.10	293.64	1.48 [c]
6	0.69	225.01	326.10	1.41 [c]

[a] Same experimental details early reported in ref.2 except 0.30 ml portions of the starting solution were diluted to 10.00 ml with benzene.

[b] Second-order rate constants ($l\ mol^{-1}\ s^{-1}$).

[c] Pseudo-first-order rate constants ($l\ mol^{-1}\ s^{-1}$).

Table 8. Typical run for reaction of *p*-chlorophenyl-4-benzal-5-pyrazolone (**3b**; 0.000765 M) with isopropyl vinyl ether (0.2261 M) in benzene at 70°

Time (sec.)	A	Reaction %	$10^3\ k_{tot}$	α	$10^4\ k_{cis}$	$10^4\ k_{trans}$
0	0.873	–	–	–	–	–
180	0.825	5.5	1.40	–	–	–
360	0.771	11.7	1.53	–	–	–
540	0.730	16.4	1.49	–	–	–
720	0.685	21.5	1.50	–	–	–
900	0.645	26.1	1.50	–	–	–
1110	0.602	31.0	1.49	–	–	–
1320	0.552	36.8	1.52	–	–	–
1530	0.529	39.4	1.49	–	–	–
1740	0.489	44.0	1.48	–	–	–
1980	0.445	49.0	1.50	3.65	11.77	3.23
2310	0.402	54.0	1.49	–	–	–
2700	0.350	59.9	1.50	–	–	–
3090	0.312	64.3	1.49	–	–	–
3600	0.265	69.6	1.48	–	–	–
After 2 days (colourless solution)				3.88	11.77	3.03

The results of a typical run are shown in Table 8 and all the details of the experimental technique were described earlier in Ref. 2.

The molar ratio $\alpha = [4]:[5]$ was determined both by the previously described TLC + UV method[2] and by a new liquid chromatography method. The residual samples from the kinetic determinations, after the soln was discoloured, were evaporated and the residue dissolved in a small volume of cyclohexane/ethyl acetate 95:5 (about 1.5 ml). Portions of 10–30 μl were injected into a Waters Associated ALC/CPC244 liquid chromatograph with a Beckman mod. 25 spectrophotometer operating at 255 nm as detector. The chromatographic separation was performed on two stainless steel columns (61 cm l. × 2 mm dia.), packing material: Corasil II 37–50 μ. The eluant, whose composition was crucial for good separation, and the experimental conditions are reported in Table 9.

Table 9. Experimental conditions used in the liquid chromatography separation of isomer mixtures

Isomers mixture	Eluant [a]	Flow rate [b]	Retention time **5**	Retention time **4**	**4** %
4,5a	96:4	0.7	4'40"	5'40"	79 ± 1.0
4,5b	95:5	0.4	6'20"	7'40"	79.5 ± 1.0
4,5c	96:4	1.0	3'30"	4'30"	78 ± 1.5
4,5d	97.5:2.5	1.0	4'10"	5'10"	79 ± 1.0
4,5e	96:4	1.7	4'10"	5'10"	80.5 ± 1.5
4,5f	97.5:2.5	0.7	4'10"	5'00"	77.5 ± 0.5

[a] Cyclohexane:etthyl acetate

[b] Ml/min.

Table 10. Half-wave reduction potentials of 1-aryl-4-benzylidene-5-pyrazolones (**3a–f**)

Pyrazolone	$-E^{red}_{1/2}$ (V.)	Slope [a]
3a	0.364	61
3b	0.371	60
3c	0.391	67
3d	0.417	69
3e	0.442	70
3f	0.399	71

[a] Slope of the plot of $-E$ (V.) vs. log $\left[i/(i_d - i)\right]$

Solns with known composition of pure **4** and **5** were prepared with a ratio of 1:1, 1:2, 1:3 and 1:5, each composition being tested on two independent samples at least five times each. A calibration curve was obtained for each couple of isomers and the unknown composition of the kinetic samples was determined by fitting the areas ratio on it. A minimum of four independent samples were tested and the error involved is believed to be small and within the limits quoted in Table 9. The molar ratio was constant throughout the reaction (Table 8).

Determination of the polarographic reduction potentials of **3**. Dimethylformamide (Erba RPE grade) was used as solvent; tetraethylammonium iodide, used as the supporting electrolyte, was stored in an oven at 60° until used. Purified N_2 was used for solns deaeration.

The polarographic curves were recorded with a pen-recording polarograph Metrohm E 506; the polarographic scan rate was 0.24 V/min. At working height of the mercury reservoir (36 cm) the capillary had m = 8.53 mg/sec and t = 1.0 sec. Internal anode was the reference electrode. All glass were carefully cleaned and dried at 100–110° for several hours immediately prior to each experiment to ensure dryness.

The half-wave potentials (reported in Table 10) are the average of at least five polarograms taken on two separate days. The maximum range was 10 mV. The values of current-potential slopes suggest that the reduction mechamism is the same in all the members of the series. The current varies linearly with the square root of mercury height on the limiting plateau, indicating that the process is diffusion controlled. The limiting current devised by the concentration is constant over a concentration range of $1 \times 10^{-4} - 1 \times 10^{-3}$ M.

The values of $E^{red}_{1/2}$ (V) give a good correlation with Hammett constants[6] and least squares and statistical treatment of the data give: slope = −0.140, intercept = 0.399 and correlation coefficient = 0.990.

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