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SUBSTITUENTS EFFECT ON THE CLAISEN REARRANGEMENT

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Abstract. The Claisen rearrangement of six homogeneous series of (R,S) or (R,R) 1,4-diaryl-6-isopropenyl-6-methyl-5,6-dihydro-4H-pyran[2,3-c]pyrazoles (**1-6**) to give 1,2-dimethyl-5-arylcyclohexene-4-spiro-4'(1'-aryl-5'-pyrazolones) (**7-12**) was kinetically investigated at 125 °C in C_6D_6. When the substituents are on the 1-aryl group (**1**,**2**) the rate increased with increases in the electron-attracting character of the substituent. When the substituents are on the 4-aryl group and the configuration is (R,S) (**3**,**5**), the rate decreased with increases in the electron-attracting character of the substituent. If the configuration is (R,R) (**4**,**6**) a lower, opposite, effect was observed. All kinetic data correlate linearly with the ϱ of the substituents. These results can be rationalized by assuming for the Claisen rearrangement a transition state having significant dipolar character, with a partial negative charge developed on the oxygenated fragment.

Even if the Claisen rearrangement is one of the best synthetic tools in carbon-carbon forming for its simplicity and selectivity,[1] some aspect of the mechanism are still argument of a serious debate. Even if a strong support for a transition state (t.s.) having significant dipolar character came from the solvent effect observed in the kinetic study of the rearrangemenet,[2-5] only few homogeneous series of substituted allyl vinyl ethers were kinetically investigated: all cyano-substituted derivatives,[6] and 4-, 5- and 6-methoxy-substituted compounds.[3]

From these kinetic data,[3,6] from the secondary deuterium isotope effect[7] and from both MNDO[8a] and AM1[8b] studies of the rearrangement, four different models of the Claisen transition state have been derived.

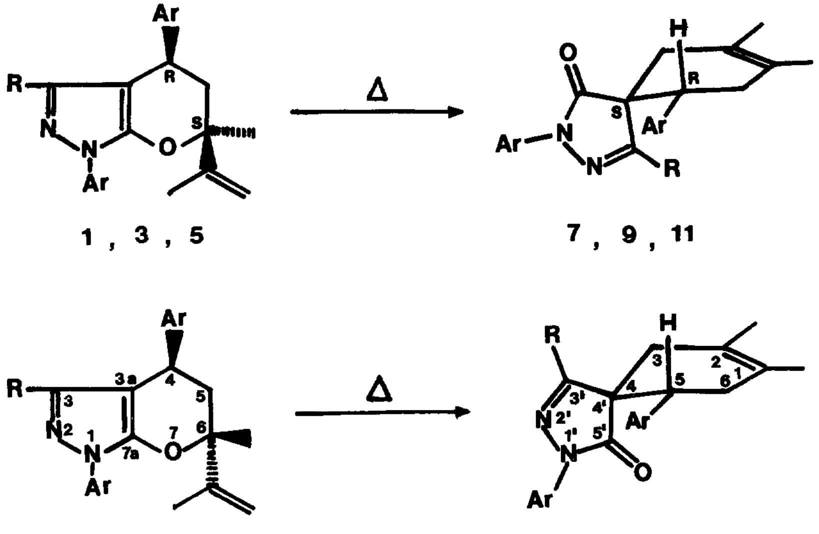
a) Dewar proposed a t.s., early described[8a] as a biradicaloid that resembles 2-oxacyclohexane-1,4-diyl with substituents favouring a polarization in the sense of a positive charge delocalized on both oxygen and the adjacent carbon atom, and later described[8b] as a species having intermediate character between aromatic and biradicaloid.
b) Gajewsky and Conrad[7] proposed an early t.s. which resembles two allyl radicals.

c) Burrows and Carpenter,[6,9] a delocalized t.s. with the phenyl anion as model.

d) Finally Coates, Curran and co-workers[3] and the Cornell group[4] proposed a pericyclic t.s. with pronounced dipolar character, the negative charge being delocalized on the oxygenated fragment. A similar t.s. can rationalize the substituent effect shown by the rearrangement of substituted cinnamylphenyl ethers.[10,11]

In a previous paper[12] we reported the results of the reaction between 1-phenyl-4-arylidene-5-pyrazolones and 2,3-dimethylbutadiene. Depending upon substituents and experimental conditions, one or both heterodienic adducts (4R,6S)[13] and (4R,6R) 1,4-diaryl-6-isopropenyl-6-methyldihydropyran[2,3-c]pyrazoles (**1,3,5** and **2,4,6** respectively) were obtained together with one or both Diels-Alder products (4S,5R) and (4R,5R) 1,2-dimethyl-5-arylcyclohexene-4-spiro-4'(1'-aryl-5'-pyrazolones) (**7,9,11** and **8,10,12** respectively). When the former ones are heated at temperatures above 100 °C,they rearrange stereospecifically to the latter ones (Scheme 1).

Scheme 1



Hence, a cleavage of the O7-C6 bond to form a dipolar intermediate was ruled out, as well as a cycloreversion (followed by recombination of arylidene-pyrazolones and dimethylbutadiene); moreover, in the presence of ethyl vinyl ether as solvent, no trace of adduct of arylidene-pyrazolone with this, which is more reactive than 2,3-dimethylbutadiene, was observed.

Thus the rearrangement of isopropyliden-dihydropyrans **1-6** to cyclohexene-spiro-pyrazolones **7-12** is a Claisen [3.3]-sigmatropic shift.

RESULTS

These rearrangements seemed suitable models to test the substituents effect on the reaction rate in a case in which they necessarily take place trough the normally less favoured boat t.s. Thus we synthesized (using our best experimental conditions to obtain them)[12] six homogeneous series (**1-6**; Scheme 2) with different (R,S) or (R,R) configurations,[14] different substituents in position 3, but, mainly, with comprehensive series of substituents in the phenyl groups either in position 1 or in position 4.

All kinetics runs were studied in C_6D_6 as solvent, in sealed tubes at 125°C, and followed to about 80% completion by ^{1}H-NMR spectroscopic analysis of the disappearing dihydropyran[2,3-c]pyrazoles **1-6** <u>versus</u> the increasing cyclohexene-spiro-pyrazolones **7-12** (see Experimental for details).

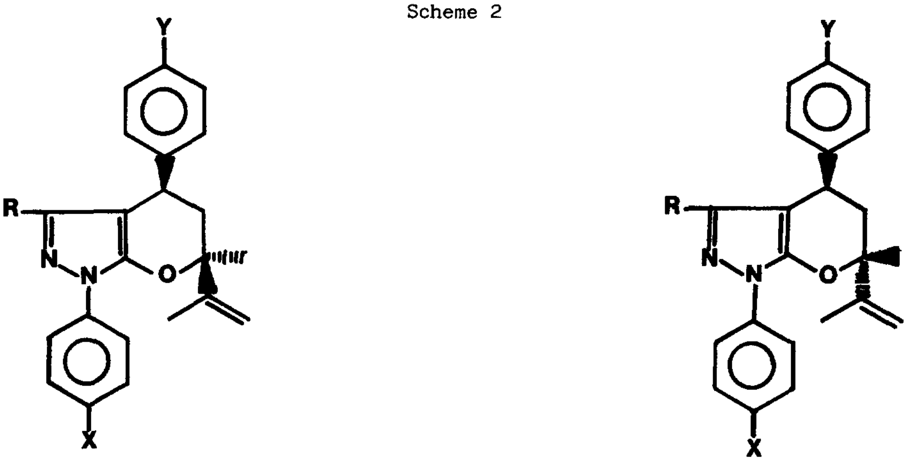
All reactions were found to follow a first order kinetic and the rate constants reported in tables 1-3 are the average of at least three kinetic runs. Only for **4a-e**, that are difficult to isolate as pure products in reasonable amounts, the k values are the average of two kinetic runs.

When the substituents are on the aryl group in position 1 (**1, 2a-f**; Table 1) the rate increased with increases in the electron-attracting character of the substituent. If log k values are plotted <u>vs</u> the σp constants of the substituent X, two linear relationships are obtained, either for (R,S) (**1a-f**) or for (R,R) (**2a-f**) isomers, (Fig. 1a) and their ρ values are nearly equal (0.55, r = 0.998 and 0.60, r = 0.995, respectively).

When the substituents are on the aryl group in position 4, a different behaviour is observed for (R,S) and (R,R) isomers (**3,5** and **4,6**, respectively; Tables 2 and 3).

In the former series the rate decreased with increases in the electron-attracting character of the Y substituent. Again if log k values are plotted <u>vs</u> the σp constants, two linear relationships are obtained, either for the 3-H-substituted series (**3a-g**) or for the 3-Me-substituted one (**5a-f** and **1d**), whose ρ values are nearly equal: -0.27, r = 0.990 and -0.29, r=0.970 respectively (Fig. 1b).

In both (R,R) series the behaviour is opposite (even if the effect is small) and a clear trend, indicating that the rate increased with increases in the electron-attracting character of the substituent, is observed. If log k values are plotted <u>vs</u> the σp constants, Scheme 2



1a : R = Me; Y = H; X = NO_2
1b : = Me; = H; = Br
1c : = Me; = H; = Cl
1d : = Me; = H; = H
1e : = Me; = H; = Me
1f : = Me; = H; = OMe

2a : R = Me; Y = H; X = NO_2
2b : = Me; = H; = Br
2c : = Me; = H; = Cl
2d : = Me; = H; = H
2e : = Me; = H; = Me
2f : = Me; = H; = OMe

3a : R = H; Y = NO_2; X = H
3b : = H; = CN; = H
3c : = H; = Cl; = H
3d : = H; = F; = H
3e : = H; = H; = H
3f : = H; = Me; = H
3g : = H; = OMe; = H

4a : R = H; Y = NO_2; X = H
4b : = H; = CN; = H
4c : = H; = Cl; = H
4d : = H; = F; = H
4e : = H; = H; = H

5a : R = Me; Y = NO_2; X = H
5b : = Me; = CN; = H
5c : = Me; = CL; = H
5d : = Me; = F; = H
5e : = Me; = Me; = H
5f : = Me; = OMe; = H

6a : R = Me; Y = NO_2; X = H
6b : = Me; = CN; = H
6c : = Me; = Cl; = H
6d : = Me; = F; = H
6e : = Me; = Me; = H
6f : = Me; = OMe; = H

again two fairly good linear relationships are obtained, either for the 3-H-substituted series (**4a–e**) or for the 3-Me-substituted one (**6a–f** and **2d**), whose ρ values are nearly equal: 0.15, r = 0.97 and 0.13, r = 0.96 respectively (Fig. 2).

DISCUSSION

We will discuss first the effect of the substituents on the aryl group in position 1. To convert dihydropyrans 1 and 2 into spiro-cyclohexenes **7** and **8**, the molecular

Table 1. Rate constants for the Claisen rearrangement of **1,2a–f** at 125°C in C_6D_6

Substituents	**1**	**2**
	10^5 x k (s^{-1})	10^5 x k (s^{-1})
a: X = NO_2	9.75 ± 0.3	4.96 + 0.09
b: = Br	4.87 ± 0.09	2.10 + 0.02
c: = Cl	4.87 ± 0.05	2.18 + 0.03
d: = H	3.42 ± 0.04	1.51 + 0.08
e: = Me	2.92 ± 0.08	1.38 + 0.01
f: = OMe	2.62 ± 0.02	1.13 + 0.04

Table 2. Rate constants for the Claisen rearrangement of **3a–g** and **4a–d** at 125°C in C_6D_6

Substituents	**3**	**4**
	10^5 x k (s^{-1})	10^5 x k (s^{-1})
a: Y = NO_2	11.6 ± 0.2	1.28 + 0.02
b: = CN	12.1 ± 0.5	1.15 + 0.02
c: = Cl	15.3 ± 0.5	0.98 + 0.04
d: = F	17.0 ± 0.5	0.97 + 0.05
e: = H	19.3 ± 0.6	0.96 + 0.09
f: = Me	21.0 ± 0.9	-
g: = OMe	21.6 ± 0.8	-

Table 3. Rate constants for the Claisen rearrangement of **5,6a–f** at 125°C in C_6D_6

Substituents	**5**	**6**
	10^5 x k (s^{-1})	10^5 x k (s^{-1})
a: Y = NO_2	1.81 ± 0.02	2.01 + 0.05
b: = CN	2.21 ± 0.02	1.95 + 0.10
c: = CN	2.61 ± 0.02	1.65 + 0.10
d: = F	2.99 ± 0.03	1.6 + 0.1
= H a)	3.42 ± 0.04 a)	1.51 + 0.08 a)
e: = Me	3.78 ± 0.05	1.60 + 0.05
f: = OMe	3.59 ± 0.04	1.45 + 0.10

a) the series are completed with data of **1d** and **2d**

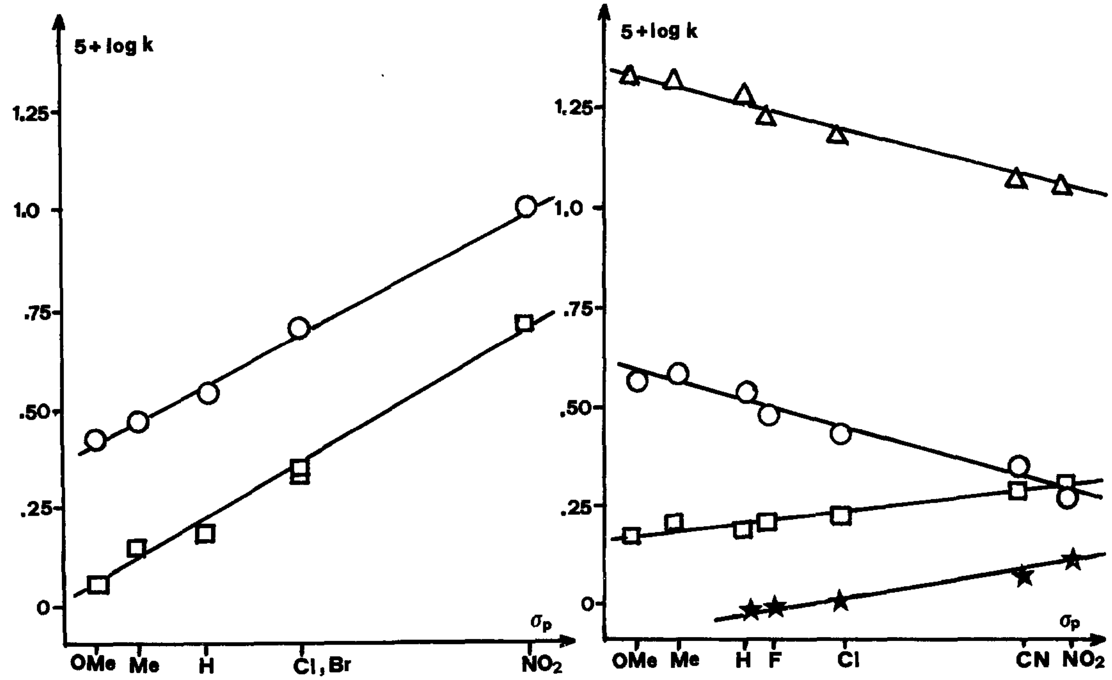


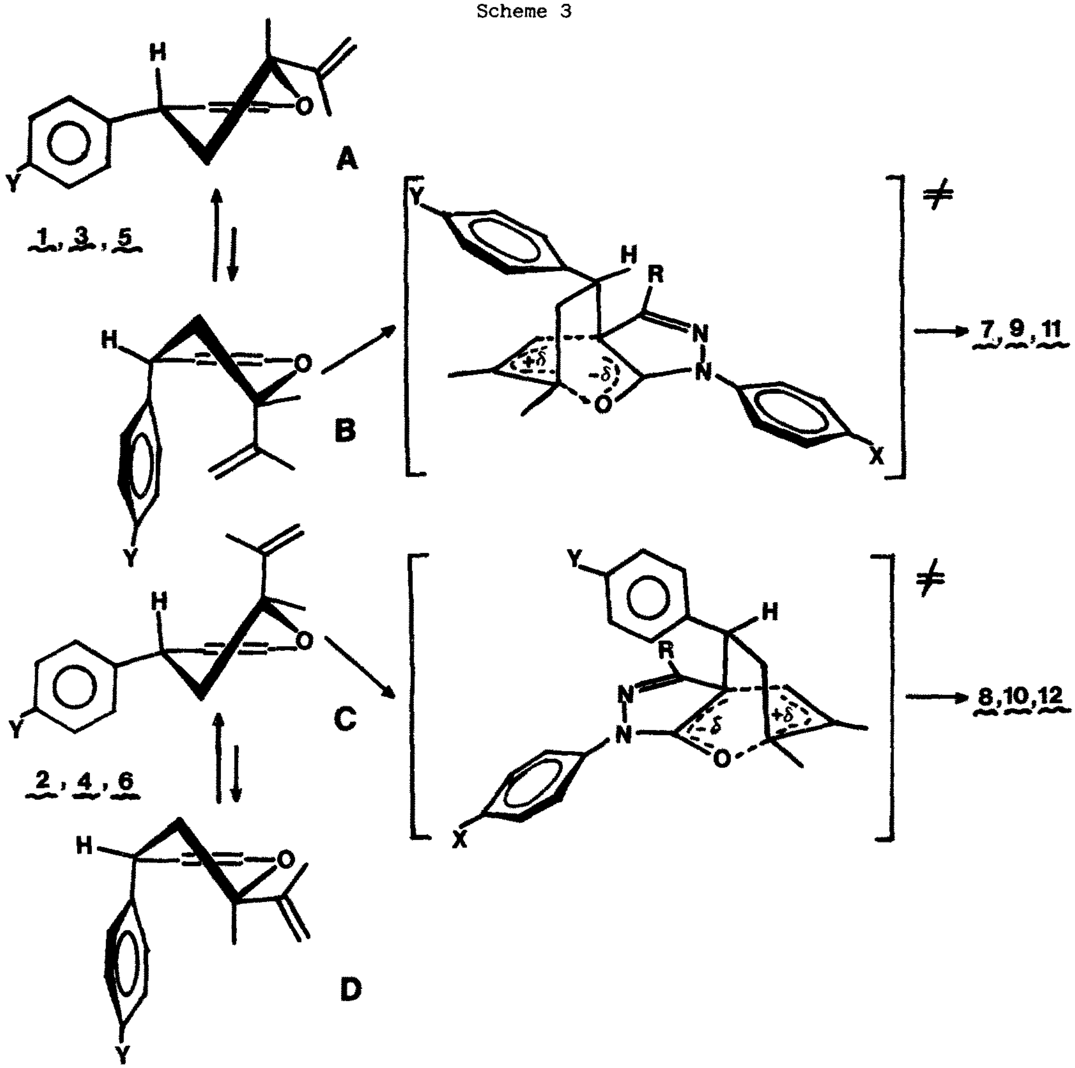
Figure 1. (a) - Rate constants of the Claisen rearrangement of **1a-f** (○) and **2a-f** (□) at 125°C in C_6D_6, plotted vs. the σp constant of the substituents.

(b) - Rate constants of the Claisen rearrangement of **3a-g** (△), **4a-e** (★), **5a-f** (○) and **6a-f** (□) (data of **1d** and **2d** are added to last two series respectively) at 125°C in C_6D_6, plotted vs the σp constant of the substituents.

framework involved requires a conformation with the isopropenyl group in an axial position to allow overlap between its π-orbital and that of the carbon atom in position 3a (Scheme 3).

From the NMR spectra of **1a-f** and **2a-f**, both series prefer conformations with the 4-phenyl group in a "pseudo-equatorial" position (the H-4 proton has a signal consistent for an axial-axial and an axial-equatorial coupling). Hence, the dihydropyran fragment of **2a-f** will adopt a half-chair conformation with the isopropenyl group in the required axial position. But **1** rearranges at a rate that is about twice faster than **2**. Thus we believe that also the isopropenyl group of **1a-f** should easily assume an axial position, and this occurs if the half-chair conformation with the isopropenyl group in the axial orientation is enough populated. In order to evaluate this possibility, MM2 calculations[15] were performed on **1d** and **2d**. The latter one showed a marked preference for conformation C (Scheme 3), the steric energy of conformation D was in fact 3.4 kcal/mole higher than that of C.

Scheme 3



On the contrary **1d** did not show a defined conformational preference, having the conformations A and B almost at the same steric energy (B was favoured over A by 0.1 kcal/mole). This result contrast with the NMR data that show a preference for an equatorial orientation of the 4-phenyl group. This discrepancy may be explained with the entropic contribution, not taken into account by MM2, that largely disfavours a diaxial orientation of both the phenyl and the isopropenyl group, owing to the severe limitations in their rotation.[16] As a consequence of this effect B becomes less populated than A; however, the non negligible amount of B existing in solution is the reactive conformation.

The effect of substituent X, that increases the reaction rate with the increase of its electron-attracting character, can be rationalized by assuming the development of a negative charge on the oxygenated fragment in the t.s. (scheme 3). Hence these results strongly support the "Coates and Curran model" of the Claisen t.s.[3]

The effect of the substituents Y on the aryl group in position 4 will now be discussed.

Figure 1b shows that the rate of the rearrangement increased with the increase of the electron-releasing effect of the substituent Y in both (R,S) series **3** and **5**. An opposite (but significantly lower) effect is observed in both (R,R) series **4** and **6**. Again this can be regarded as a clear evidence in favour of the "Coates and Curran model".[3]

The t.s. involved in the conversion of both (R,S) series **3** and **5** (Scheme 3) has the Y-substituted phenyl ring overlapping the positively polarized fragment. Thus electron-releasing substituents will stabilize the positive charge either by a through-space "donor-acceptor" interaction or by a favourable electrostatic effect. The opposite interaction, involving the negatively polarized fragment and the overlapping (but somewhat twisted, if the more stable conformation[18] of the starting product is retained in the t.s) aryl group, rationalizes the opposite (but weakened) behaviour of both (R,R) series **4** and **6**.

Finally the relative rates of **3** vs. **5** and **4** vs. **6** can be rationalized as follows. Going from **3** and **5** to their t.s.s, as the orbital of the terminal olefinic carbon of the isopropenyl group overlaps the orbital of C-3a, the aryl group in position 4 moves to increase its steric interaction with R (Scheme 4). Thus the rate of **3** (R=H) is expected to be greater than that of **5** (R = Me).[19]

On the contrary, when **4** and **6** moove to their t.s.s, as the isopropenyl group overlaps C-3a, a relief of the steric hindrance between the aryl group in 4 and R occurs (Scheme 4). Thus the rate of **4** (R=H) is expected to be smaller than that of **6** (R=Me).[19]

In conclusion, the rate of the Claisen rearrangement seems to be a function of both the stabilization of the charges developed in the t.s. and of the steric crowding of this.

Scheme 4

3, **5**

4, **6**

EXPERIMENTAL

Melting points, uncorrected, were determined by the capillary method on a Tottoli apparatus. Elemental analyses were made on Erba CHN analyzer mod. 1106. IR Spectra (nujol mulls) were recorded on a Perkin-Elmer 983 spectrophotometer; ^{1}H-NMR spectra on a Bruker WP80 SY spectrometer (chemical shifts in ppm on the scale, coupling constants in Hz).

1-Phenyl-4-aryliden-5-pyrazolones. Prepared in accord with the literature method.[20,21]

1-Phenyl-3-methyl-4-aryliden-5-pyrazolones. Prepared in accord with the literature method.[20]

1-Aryl-4-bezyliden-3-methyl-5-pyrazolones. Prepared in accord with the literature method.[22-25] Analogously 1-p.tolyl-3-methyl-4-benzyliden-5-pyrazolone was prepared from benzaldehyde and 1-p.tolyl-3-methyl-5-pyrazolone as red needles (55%), m.p. 101-102 °C (EtOH) (Found: C, 78.4; H, 5.7; N, 10.1%. Calc. for $C_{18}H_{16}N_2O$: C, 78.2, H, 5.8; N, 10.1%).

Preparations of compounds **1-6**. These products were prepared from the CF_3COOH catalyzed reaction of 1-aryl-4-aryliden-5-pyrazolones and 2,3-dimethylbutadiene following the procedure described in ref. 12. The operations required to separate these adducts are reported hereto.

a) From 3-H pyrazolones the spent reaction mixture was column chromatographed (Silic agel Merck 230-400 mesh, eluant methylene chloride) and pure **9a-g** was obtained as first fraction. The second fraction (**3a-g** and **4a-g** in admixture) was submitted to medium pressure liquid chromatography (Miniprep Jovin Yvon, Silica gel Merck 0.063 mm., eluant cyclohexane ethyl acetate 98:2) and pure **4a-g** and **3a-g** were obtained in the order.

b) From 3-Me pyrazolones the spent reaction mixture was column chromatographed (Silica gel Merck 230-400 mesh, eluant methylene chloride) and the dienic cycloadducts (**7** and **8** or **11** and **12** in admixture) were obtained as first fraction and the heterodienic ones (**1** and **2** or **5** and **6** in admixture) as the second fraction. These latter mixtures were submitted to medium pressure liquid chromatography (same conditions as in a) and pure **2a-f** and **1a-f** (respectively **6a-f** and **5a-f**) were obtained in the order. The physical characteristics and the NMR spectra of compounds **1-6** not previously described,[12] are reported in tables 4 and 5.

[3.3] Sigmatropic rearrangement of **1-6** to **7-12**. General procedure. A mixture of 0.5 mmoles of **1-6** (0.05 mmoles for **4a-e**) and 5 mL. of dry benzene was heated on an oil bath at 125 °C in a sealed tube until the starting product completely disappeared (TLC, CH_2Cl_2 as eluant). After evaporation of the solvent, the corresponding **7-12** isomers were isolated in nearly quantitative yield. The physical characteristics and the NMR spectra of compounds **7-12**, not previously described,[12] are reported in tables 6 and 7.

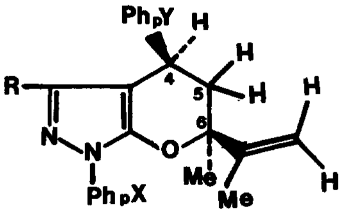
Kinetics. A 0.1 molar C_6D_6 solution of the required dihydropyran (**1-6**) in a sealed NMR tube, was placed at time zero in an oil ultrathermostat at 125±0.2 °C. At appropriate time intervals (from 30 minutes to 5 hours depending on the rate of the rearrangement) the tube was quickly cooled at room temperature and the ^{1}H-NMR was registered on a Bruker WP80 SY spectrometer. The relative concentrations of |**7-12**| versus |**1-6**| were determined from the integrals ratios of the H-5 benzylic proton of the developing product versus the H-4 benzylic proton of the disappearing starting material. These values were checked by measuring the ratio of the H-5 integral vs the integral of each of the two vinylic protons of (**1-6**). The riproducibility of the values was in the range ± 3%. Each kinetic determination consisted of at least six measures in the range 15-80% conversion, and the rate constants are the average of at least three kinetic runs (two for **4a-c**).

Table 4. Physical data of compounds **1-6**

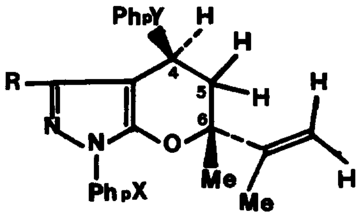
Compd	Yield	M.p. (solv.)	Elemental analyses				
1a	15	149-151° (a)	for $C_{23}H_{23}N_3O_3$	calc.:	C, 70.9;	H, 5.9;	N, 10.8%
				found:	71.1;	6.0	10.9
2a	23	162-163° (a)		found:	70.7;	5.9;	10.7
1b	20	156-157° (b)	for $C_{23}H_{23}BrN_2O$	calc.:	C, 65.2;	H, 5.5.;	N, 6.6%
				found:	65.4;	5.3;	6.5
2b	32	129-130° (b)		found:	65.5;	5.6;	6.6
5b	23	161-162° (c)	for $C_{24}H_{23}N_3O$	calc.:	C, 78.0;	H, 6.3;	N, 11.4%
				found:	77.7;	6.2;	11.3
6b	35	171-172° (c)		found:	78.3;	6.3;	11.5
1c	21	163-164° (c)	for $C_{23}H_{23}ClN_2O$	calc.:	C, 72.9;	H, 6.1;	N, 7.4%
				found:	72.7;	6.2;	7.3
2c	34	153-154° (c)		found:	72.9;	6.2;	7.3
5c	18	146-147° (c)		found:	72.6;	6.0;	7.4
6c	27	124-125° (c)		found:	73.0;	6.2;	7.4
5d	25	118-119° (c)	for $C_{23}H_{23}FN_2O$	calc.:	C, 76.2;	H, 6.4;	N, 7.7%
				found:	76.3;	6.3;	7.7
6d	35	99-100° (c)		found:	76.3;	6.4;	7.6
1e	25	129-130° (d)	for $C_{24}H_{26}N_2O$	calc.:	C, 80.4;	H, 7.3;	N, 7.8%
				found:	80.6;	7.3;	7.9
2e	35	131-132° (d)		found:	80.6;	7.4;	7.9
5e	21	131-133° (c)		found:	80.2;	7.2;	7.7
6e	28	103-104° (a)		found:	80.7;	7.2;	7.7
1f	17	134-135° (c)	for $C_{24}H_{26}N_2O_2$	calc.:	C, 77.0;	H, 7.0;	N, 7.5%
				found:	76.7;	6.9;	7.4
2f	25	124-125° (c)		found:	77.2;	7.1;	7.5
5f	22	124-125° (c)		found:	77.2	6.9;	7.4
6f	32	127-128° (c)		found:	77.2;	7.1;	7.6
3c	35	153-154° (b)	for $C_{22}H_{21}ClN_2O$	calc.:	C, 72.4;	H, 5.8;	N, 7.7%
				found:	72.5;	5.8;	7.7
4c	5	142-143° (b)		found:	72.2;	5.7;	7.8
3d	38	111-112° (c)	for $C_{22}H_{21}FN_2O$	calc.:	C, 75.8;	H, 6.1;	N, 8.0%
				found:	75.7;	6.2;	7.9
4d	7	104-105° (c)		found:	75.6;	6.1	8.2
3f	35	130-131° (b)	for $C_{23}H_{24}N_2O$	calc.:	C, 80.2;	H, 7.0;	N, 8.1%
				found:	80.4;	7.1;	8.0
4f	5	oil		found:	80.6;	7.3;	7.9

(a) EtOH.(b) Diisopropyl ether.(c) Petroleum ether 60-80°.(d) Cyclohexane.

Table 5. ^{1}H-NMR(a) spectra of compounds **1-6**



1, 3, 5



2, 4, 6

Compd	H-4(b)	5-CH_2(c)	CH_2 Vinylic(d)		6-Me(e)	Me (d)	R(e)	X/Y(e)
1a	3.68	1.82	5.05	4.8	1.20	1.57	1.86	--
2a	3.65	1.5-2.25	4.85	4.75	1.30	1.5	1.77	--
1b	3.74	1.6-1.9	5.07	4.8	1.21	1.58	1.93	--
2b	3.7	1.5-2.25	4.92	4.78	1.3	1.53	1.85	--
1c	3,72	1.5-2.0	5.05	4.77	1.20	1.55	1.9	--
2c	3.7	1.5-2.25	4.9	4.75	1.27	1.51	1.82	--
1e	3.78	1.85	5.15	4.8	1.23	1.6	1.97	2.08
2e	3.75	1.60-2.25	4.98	4.77	1.33	1.55	1.9	2.08
1f	3.80	1.87	5.15	4.80	1.25	1.6	1.98	3.3
2f	3.77	1.6-2.3	5.0	4.80	1.33	1.56	1.90	3.3
3c	3.68	1.3-2.0	5.15	4.85	1.21	1.65	(f)	--
4c	3.6	1.3-2.1	4.95	4.76	1.3	1.52	(f)	
3d	3.65	1.4-1.9	5.10	4.80	1.18	1.60	(f)	--
4d	3.58	1.3-2.0	4.88	4.70	1.26	1.46	(f)	--
3f	3.83	1.83	5.14	4.82	1.23	1.65	(f)	2.20
4f	3.75	1.3-2.1	4.95	4.75	1.3	1.52	(f)	2.18
5b	3.6	1.4-1.9	5.12	4.82	1.21	1.58	1.82	--
6b	3.58	1.35-2.1	4.92	4.77	1.32	1.58	1.74	--
5c	3.64	1.4-1.9	5.14	4.82	1.24	1.62	1.92	--
6c	3.56	1.3-2.1	4.9	4.72	1.25	1.47	1.75	--
5d	3.70	1.6-2.1	5.18	4.85	1.25	1.63	1.95	--
6d	3.60	1.2-2.1	4.9	4.73	1.27	1.5	1.8	--
5e	3.84	1.93	5.18	4.85	1.28	1.65	2.05	2.22
6e	3.78	1.6-2.3	5.0	4.8	1.35	1.58	1.96	2.22
5f	3.82	1.93	5.2	4.88	1.3	1.67	2.04	3.42
6f	3.73	1.6-2.3	4.95	4.75	1.30	1.53	1.9	3.35

(a) In C_6D_6. (b) Doubling doublet; triplet for **1a**, **e**, **f**, **3f**, **5e**,**f**; J_{45} + $J_{45'}$, are always in the range 15-17 Hz. (c) Doublet for **1a**, **e**, **f**, **3f**, **5e**,**f**; multiplet for the others. (d) Broad singlet. (e) Singlet. (f) Overlapped by aromatics.

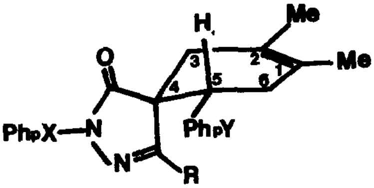
Table 6. Physical data of compounds 7-12

Compd	Yield[a)]	M.p. (solv.)	Elemental analyses					I.R (C=O) cm^{-1}
7a	10	146-7° (c)	for $C_{23}H_{23}N_3O_3$	calc.:	C,70.9;	H,5.9;	N,10.8%	
				found:	70.6;	5.7;	10.7	1709
8a	20	212-3° (c)		found:	70.7;	5.8;	10.6	1716
7b	13	118-9° (c)	for $C_{23}H_{23}BrN_2O$	calc.:	C,65.2;	H,5.5;	N, 6.6%	
				found:	64.8;	5.5;	6.5	1711
8b	22	146-7° (c)		found:	65.2;	5.3;	6.5	1703
11b	10	165-7° (c)	for $C_{24}H_{23}N_3O$	calc.:	C,78.0;	H,6.3;	N,11.4%	
				found:	78.2;	6.1;	11.2	1700
12b	25	143-4° (c)		found:	77.8;	6.1;	11.5	1700
7c	12	103-4° (c)	for $C_{23}H_{23}ClN_2O$	calc.:	C,72.9;	H,6.1;	N,7.4%	
				found:	72.5;	6.1;	7.3	1709
8c	20	151-2° (c)		found:	73.0;	6.2;	7.3	1703
11c	15	172-3° (c)		found:	72.9;	6.0;	7.5	1705
12c	25	178-9° (c)		found:	72.7;	6.2;	7.4	1709
11d	10	127-8° (c)	for $C_{23}H_{23}FN_2O$	calc.:	C,76.2;	H,6.4;	N,7.7%	
				found:	76.4;	6.4;	7.6	1710
12d	17	162-3° (c)		found:	76.2;	6.5;	7.6	1710
7e	10	87-8° (c)	for $C_{24}H_{26}N_2O$	calc.:	C,80.4;	H,7.3;	N,7.8%	
				found:	80.3;	7.4;	7.7	1710
8e	18	132-3° (c)		found:	80.7;	7.4;	7.9	1705
11e	12	159-60° (c)		found:	80.4;	7.2;	7.7	1709
12e	25	144-5° (c)		found:	80.2;	7.4;	7.6	1710
7f	15	118-9° (c)	for $C_{24}H_{26}N_2O_2$	calc.:	C,77.0;	H,7.0;	N,7.5%	
				found:	76.8;	7.1;	7.6	1696
8f	25	124-5° (c)		found:	77.0;	7.0;	7.6	1692
11f	10	129-30° (d)		found:	76.7;	7.0;	7.5	1710
12f	20	120-21° (d)		found:	76.8;	6.9;	7.6	1710
10a	(b)	142-3° (c)	for $C_{22}H_{21}N_3O_3$	calc.:	C,70.4;	H,5.6;	N,11.2%	
				found:	70.3;	5.8;	11.0	1710
10b	(b)	141-3° (d)	for $C_{23}H_{21}N_3O$	calc.:	C,77.7;	H,6.0;	N,11.8%	
				found:	78.0;	6.2;	11.6	1706
9c	40	153-4° (d)	for $C_{22}H_{21}ClN_2O$	calc.:	C,72.4;	H,5.8;	N,7.7%	
				found:	72.2;	5.9;	7.6	1710
10c	(b)	83-4° (c)		found:	72.7;	6.0;	7.6	1700
9d	39	97-8° (c)	for $C_{22}H_{21}FN_2O$	calc.:	C,75.8;	H,6.1;	N,8.0%	
				found:	75.7;	6.0;	8.1	1695
10d	(b)	129-30° (c)		found:	75.9;	6.2;	7.9	1700
10e	(b)	130-31° (c)	for $C_{22}H_{22}N_2O$	calc.:	C,80.0;	H,6.7;	N,8.5	
				found:	80.3;	6.9;	8.4	1705
9f	40	120-21° (d)	for $C_{23}H_{24}N_2O$	calc.:	C,80.2,	H,7.0;	N,8.1	
				found:	80.1;	7.0;	8.0	1704

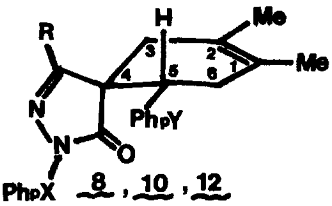
(a) The reported yields are from the CF_3COOH-catalyzed reaction of 1-aryl-4-arylidene-5 – pyrazolones and 2,3-dimethylbutadiene; the yields from the [3.3] sigmatropic rearrangement are nearly quantitative.

(b) Obtained from the [3.3] sigmatropic rearrangement only. (c) EtOH. (d) Diisopropyl ether.

Table 7. ^{1}H-NMR$^{(a)}$ spectra of compounds 7-12



7, **9**, **11**



8, **10**, **12**

Compd	$H_5^{(b)}$	$3\text{-}CH_2,6\text{-}CH_2$	$Me^{(c)}$	$R^{(d)}$	$X/Y^{(d)}$
7a	3.20	1.1-2.9	1.40	1.86	--
8a	2.60	1.1-2.25,3.2$^{(e)}$	1.52 1.65	1.58	--
7b	3.28	1.1-2.9	1.45	1.90	--
8b	2.65	1.1-2.25,3.25$^{(e)}$	1.53 1.65	1.60	--
7c	3.28	1.1-2.9	1.45	1.92	--
8c	2.63	1.1-2.25,3.25$^{(e)}$	1.52 1.65	1.60	--
7e	3.33	1.1-2.9	1.43	1.97	1.95
8e	2.70	1.1-2.35,3.34$^{(e)}$	1.55 1.67	1.65	2.05
7f	3.37	1.1-2.9	1.45	1.98	3.22
8f	2.70	1.1-2.25, 3.32$^{(e)}$	1.55 1.66	1.66	3.25
9a	3.05	1.0-2.75	1.43	(f)	--
10a	2.55	1.0-2.2,2.95$^{(e)}$	1.50 1.62	6.65	--
9b	3.02	1.0-2.75	1.43	(f)	--
10b	2.55	1.1-2.25, 3.0$^{(e)}$	1.52 1.64	6.65	--
9c	3.07	1.1-2.8	1.43	(f)	--
10c	2.60	1.1-2.25,3.08$^{(e)}$	1.50 1.62	6.67	--
9d	3.13	1.1-2.9	1.45	(f)	--
10d	2.62	1.1-2.25,3.10$^{(e)}$	1.50 1.62	(f)	--
9e	3.21	1.1-2.9	1.45	(f)	--
10e	2.72	1.1-2.25,3.25$^{(e)}$	1.50 1.62	6.72	--
9f	3.25	1.1-2.9	1.45	(f)	1.92
9g	3.25	1.1-2.9	1.47	(f)	3.15
11b	3.12	1.1-2.9	1.40	1.82	--
12b	2.45	1.1-2.2,3.07$^{(e)}$	1.50 1.62	1.50	--
11c	3.20	1.1-2.9	1.43	1.86	--
12c	2.55	1.2-2.25,3.20$^{(e)}$	1.52 1.66	1.57	--
11d	3.23	1.1-2.9	1.45	1.90	--
12d	2.58	1.2-2.25,3.35$^{(e)}$	1.54 1.68	1.60	--
11e	3.35	1.1-2.9	1.45	1.92	1.98
12e	2.70	1.2-2.25,3.35$^{(e)}$	1.55 1.65	1.65	1.92
11f	3.35	1.1-2.9	1.45	1.98	3.15
12f	2.70	1.2-2.3,3.33$^{(e)}$	1.55 1.67	1.67	3.15

(a) In C_6D_6.(b) Doubling doublet; J_{56} + $J_{56'}$ are always in the range 15.5-18.5 Hz. (c) Broad singlet(s); broad triplet for **9a–d**. d) Singlet. (e) 1H, broad triplet. (f) Overlapped by aromatics.

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19 (R,S) and (R,R) 1,3,4-triphenyl-6-isopropenyl-6-methyldihydropyran[2,3-c]pyrazoles have been synthesized and their rearrangement rates were determined at 125° C in C_6D_6. The $k(s^{-1})$ were $1.07 \pm 0.07 \times 10^{-5}$ and $4.01 \pm 0.09 \times 10^{-5}$ respectively. If the former value is compared with k values of **1d** and **3e**, rate lies in the order: 3-H > 3-Me > 3-Ph. If the latter value is compared with k values of **2d** and **4e**, rate lies in the order: 3-Ph > 3-Me > 3-H. In both cases the new data support the rationalization proposed in the text.

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