# Structure of 5-Methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones

# Jean E. Rockley<sup>A</sup> and Lindsay A. Summers<sup>A,B</sup>

<sup>A</sup> Department of Chemistry, University of Newcastle, N.S.W. 2308. <sup>B</sup> Author to whom correspondence should be addressed.

### Abstract

5-Methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones have been synthesized. Of the 12 possible tautomeric forms it has been shown that they exist as the (arylamino)methylene tautomer with intramolecular hydrogen bonding between the CO and exocyclic NH groups.

There has been considerable interest and controversy over the past two decades in the tautomerism of 4-arylhydrazono-3-methylisoxazol-5-ones and related 4-arylhydrazono-3-methyl-1*H*-pyrazol-5-ones. 4-Arylhydrazono-3-methylisoxazol-5-ones are formally capable of existence in four tautomeric forms (1), (2), (3) and (4). In connection with work on the fungicide drazoxolon (4-o-chlorophenylhydrazono-3methylisoxazol-5-one<sup>1,2</sup>) it was established that they exist essentially as the tautomer (1) with intramolecular hydrogen bonding between the CO and NH groups.<sup>3,4</sup> This view was subsequently confirmed by other workers<sup>5</sup> and is in accord with recent molecular orbital calculations.<sup>6</sup> An earlier claim that the 4-arylhydrazono-3-methylisoxazol-5-ones exist as structure (3)<sup>7,8</sup> was shown to be incorrect<sup>9</sup> and was due, in part, to erroneous structural assignments.

Likewise 1-aryl(or alkyl)-4-arylhydrazono-3-methyl-1*H*-pyrazol-5-ones are formally capable of existence in the four tautomeric forms (5), (6), (7) and (8) with R = aryl or alkyl. The structure of the dyestuff 3-methyl-1-phenyl-4-phenylhydrazono-1*H*-pyrazol-5-one and closely related compounds in particular have been the subject of

- <sup>3</sup> Summers, L. A., and Shields, D. J., Chem. Ind. (London), 1964, 1264.
- <sup>4</sup> Summers, L. A., Freeman, P. F. H., and Shields, D. J., J. Chem. Soc., 1965, 3312.
- <sup>5</sup> Snavely, F. A., and Yoder, C. H., J. Inorg. Nucl. Chem., 1971, 33, 2699.
- <sup>6</sup> Parkanyi, C., and Shawali, A. S., J. Heterocycl. Chem., 1980, 17, 897.
- <sup>7</sup> Cum, G., Lo Vecchio, G., and Aversa, M. C., Gazz. Chim. Ital., 1965, 95, 583.
- <sup>8</sup> Cum, G., Lo Vecchio, G., Aversa, M. C., and Crisafulli, M., *Gazz. Chim. Ital.*, 1967, **97**, 346. <sup>9</sup> Summers, L. A., *Experientia*, 1966, **22**, 499.

<sup>&</sup>lt;sup>1</sup> Summers, L. A., Freeman, P. F. H., Geoghegan, M. J. A., and Turner, J. A. W., Br. Pat. 999,097 (1965).

<sup>&</sup>lt;sup>2</sup> Worthing, C. R., (Ed.), 'The Pesticide Manual' 6th Edn, p. 228 (The British Crop Protection Council: Croydon, England, 1979).





much study. Although early reports favoured structure (6; R = Ph)<sup>10-12</sup> or structure (8; R = Ph)<sup>13</sup> it has now been conclusively established<sup>14-27</sup> that the dyestuff exists as the phenylhydrazono tautomer (5; R = Ph) with intramolecular hydrogen bonding between the CO and NH groups, although not unexpectedly in basic and highly polar solvents other forms are also present (e.g. refs<sup>20,26</sup>). 1,3-Dimethyl-4-phenylhydrazono-1*H*-pyrazol-5-one similarly exists as tautomer (5; R = Me).<sup>17</sup> In the case of 3-methyl-4-phenylhydrazono-1*H*-pyrazol-5-one there are in addition to tautomers (5; R = H), (6; R = H), (7; R = H) and (8; R = H) eight other possible structures (9), (10), (11), (12), (13), (14), (15) and (16). 3-Methyl-4-phenylhydrazono tautomer (5; R = H)<sup>17,23</sup> although structures (9)–(16) were not considered.

Closely akin to the 4-arylhydrazono compounds are the corresponding 4-(arylamino)methylene analogues which likewise can exist in similar tautomeric forms. In the isoxazolone series it has been established that 3-methyl-4-(phenylamino)methyleneisoxazol-5(4*H*)-one exists as the (phenylamino)methylene tautomer (17) with intramolecular hydrogen bonding between the CO and NH groups.<sup>28,29</sup> In the pyrazolone series 5-methyl-2-phenyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*pyrazol-3-one likewise exists as the (phenylamino)methylene tautomer (18;

- <sup>10</sup> Yasuda, H., Sci. Pap. Inst. Phys. Chem. Res. (Jpn), 1962, 56, 267 (Chem. Abstr., 1963, 58, 12087).
- <sup>11</sup> Snavely, F. A., Trahanovsky, W. S., and Suydam, F. H., J. Org. Chem., 1962, 27, 994.
- <sup>12</sup> Bekarek, V., Dobas, I., Socha, J., Vetesnik, P., and Vecera, M., Collect. Czech. Chem. Commun., 1970, **35**, 1406 (Chem. Abstr., 1970, **73**, 13709).
- <sup>13</sup> Pelz, W., Püschel, W., Schellenberger, H., and Löffler, K., Angew. Chem., 1960, 72, 967.
- <sup>14</sup> Toda, S., Nippon Kagaku Zasshi, 1959, 80, 402 (Chem. Abstr., 1961, 55, 4150).
- <sup>15</sup> Jones, R., Ryan, A. J., Sternhell, S., and Wright, S. E., *Tetrahedron*, 1963, 19, 1497.
- <sup>16</sup> Kaul, B. L., Nair, P. M., Rao, A. V. R., and Venkataraman, K., Tetrahedron Lett., 1966, 3897.
- <sup>17</sup> Elguero, J., Jacquier, R., and Tarrago, G., Bull. Soc. Chim. Fr., 1966, 2990.
- <sup>18</sup> Yasuda, H., and Midorikawa, H., J. Org. Chem., 1966, 31, 1722.
- <sup>19</sup> Snavely, F. A., and Yoder, C. H., J. Org. Chem., 1968, 33, 513.
- <sup>20</sup> Lestina, G. J., and Regan, T. H., J. Org. Chem., 1969, 34, 1685.
- <sup>21</sup> Yasuda, H., Bull. Chem. Soc. Jpn, 1967, 40, 1239 (Chem. Abstr., 1967, 67, 48707).
- <sup>22</sup> Yasuda, H., Appl. Spectrosc., 1969, 23, 22.
- <sup>23</sup> Arriau, J., Campillo, J. P., Elguero, J., and Pereillo, J. M., Tetrahedron, 1974, 30, 1345.
- <sup>24</sup> Arriau, J., Campillo, J. P., Deschamps, J., and Parmentier, P., Tetrahedron, 1974, 30, 1353.
- <sup>25</sup> Ioffe, I. S., Kryukova, L. M., and Kim, N.Y., Zh. Org. Khim., 1971, 7, 2193 (Chem. Abstr., 1972, 76, 45638).
- <sup>26</sup> Trotter, P. J., Appl. Spectrosc., 1977, 31, 30.
- <sup>27</sup> Parent, R. A., J. Soc. Dyers Colour., 1976, 92, 371 (Chem. Abstr., 1977, 86, 30980).
- <sup>28</sup> Summers, L. A., Aust. J. Chem., 1973, 26, 889.
- <sup>29</sup> Maquestiau, A., Van Haverbeke, Y., and Muller, R. N., J. Heterocycl. Chem., 1975, 12, 27.

R = Ph)<sup>30-37</sup> of the four possible forms (18; R = Ph), (19; R = Ph), (20; R = Ph) and (21; R = Ph) with intramolecular hydrogen bonding between the CO and NH groups<sup>30-33,35-37</sup> although other forms may be present in highly polar solvents<sup>32,36</sup> or at low temperatures.<sup>37</sup> An X-ray crystallographic study of 5-methyl-2-phenyl-4-[(*o*-methylthiophenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one has confirmed that it exists as the analogous (phenylamino)methylene tautomer.<sup>38</sup> 2,5-Dimethyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one also has the (phenylamino)methylene structure (18; R = Me).<sup>31,32</sup>

This paper is concerned with the synthesis of 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones, which have not so far been studied, and with an investigation designed to determine the dominant tautomer(s) from the 12 possible structures (18; R = H), (19; R = H), (20; R = H), (21; R = H), (22), (23), (24), (25), (26), (27), (28) and (29).

Table 1.5-Methyl-4-[(arylamino)methylene]-2,4-dihydro-3H-pyrazol-3-ones (18; R = H)Solvent of recrystallization is ethanol

Aryl	M.p.	Molecular	Fo	ound (	(%)	Requires (%)			
group	(°C)	formula	• • <b>C</b>	н	N	C	н	Ν	
Phenyl	210 <sup>A</sup>	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O	65.6	5.3	20.9	65.6	5.5	20.9	
2-Chlorophenyl	210	$C_{11}H_{10}ClN_{3}O$	55.6	4.3	17.9	56.0	4.3	17.8	
3-Chlorophenyl	204	$C_{11}H_{10}ClN_3O$	55.8	4.3	17.5	56.0	4.3	17.8	
4-Chlorophenyl	204	$C_{11}H_{10}ClN_3O$	56.3	4 · 3	18.2	56.0	4.3	17.8	

<sup>A</sup> Moyer and Dains<sup>39</sup> reported m.p. 204° for their impure product.

5-Methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones, which are listed in Table 1, were prepared by the reaction of 5-methyl-2,4-dihydro-3*H*-pyrazol-3-one with the appropriate N,N'-diarylmethanimidamide. This reaction had been studied earlier by Moyer and Dains<sup>39</sup> who found that 5-methyl-2,4-dihydro-3*H*-pyrazol-3one reacted with difficulty with N,N'-diphenylmethanimidamide. They isolated a product which they considered to be 5-methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one but only the nitrogen elemental analysis was reported and this was well outside acceptable limits. 5-Methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones are yellow crystalline solids which are slightly soluble in water. They are stable in dilute acid solution but are much less stable in alkali.

- <sup>36</sup> Freyer, W., and Radeglia, R., Monatsh. Chem., 1978, 109, 1093.
- <sup>37</sup> Freyer, W., J. Prakt. Chem., 1978, 320, 521.
- 38 Wolfbeis, O. S., and Ziegler, E., Z. Naturforsch., Teil B, 1977, 32, 1077.
- <sup>39</sup> Moyer, H. V., and Dains, F. B., J. Am. Chem. Soc., 1928, 50, 2293.

<sup>&</sup>lt;sup>30</sup> Kurkovskaya, L. N.; Shapet'ko, N. N., Kvitko, I. Y., and Koshelev, Y. N., *Zh. Org. Khim.*, 1972, **8**, 215 (*Chem. Abstr.*, 1972, **76**, 112550).

<sup>&</sup>lt;sup>31</sup> Kurkovskaya, L. N., Shapet'ko, N. N., Kvitko, I. Y., Koshelev, Y. N., and Sof'ina, E. M., *Zh. Org. Khim.*, 1973, **9**, 821 (*Chem. Abstr.*, 1973, **79**, 4728).

<sup>&</sup>lt;sup>32</sup> Kurkovskaya, L. N., Shapet'ko, N. N., Kvitko, I. Y., Koshelev, Y. N., and Smartseva, E. D., *Zh. Org. Khim.* 1974, **10**, 2210 (*Chem. Abstr.*, 1975, **82**, 30821).

<sup>&</sup>lt;sup>33</sup> Kurkovskaya, L. N., Shapet'ko, N. N., Samartseva, E. D., Koshelev, Y. N., Sof'ina, E. M., and Kvitko, I. Y., *Zh. Org. Khim.*, 1975, **11**, 1734 (*Chem. Abstr.*, 1975, **83**, 193166).

<sup>&</sup>lt;sup>34</sup> Maquestiau, A., Van Haverbeke, Y., and Vanovervelt, J. C., *Bull. Soc. Chim. Belg.*, 1975, **84**, 741. <sup>35</sup> Freyer, W., *J. Prakt. Chem.*, 1978, **320**, 508.

The salient spectral features of the 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones are recorded in Table 2. There was no evidence for the presence of more than one tautomer. The presence of a strong band due to CO stretching at about 1670 cm<sup>-1</sup> in the infrared spectra of all four compounds eliminates the tautomeric structures (21;  $\mathbf{R} = \mathbf{H}$ ), (24), (26), (27), (28) and (29) from consideration since these structures contain no carbonyl group. The ultraviolet absorption spectra show a strong absorption band at about 370 nm (log  $\varepsilon$  c. 4.25) due to the presence of conjugated chromophores. This eliminates structure (19) which has incompletely conjugated chromophores. In the <sup>1</sup>H n.m.r. spectra there are no signals which can be attributed to the CH groups at positions 4 and 5 in structure (22) and position 5 in structure (23) or to the methylene group in structure (25). Structures (22), (23) and (25) are, therefore, eliminated from consideration. This leaves structure (18;  $\mathbf{R} = \mathbf{H}$ ) or structure (20;  $\mathbf{R} = \mathbf{H}$ ) as the possible tautomeric forms for 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones.

Tab	le 2. 5	Spectra	a of	5-me	ethyl-4-	[(ary	lamir	10)methyl	ene]-2,4-di	hyd	lro-3 <i>H-</i> pyra	zol-3	-ones (18	i; 🗋	$\mathbf{R} = \mathbf{H}$
I.r.	spectra	were	run	in a	a KBr	disc	or i	1 CHCl <sub>3</sub>	solution,	as	indicated;	u.v.	spectra	in	CHCl <sub>3</sub> ;
						3	n.m.1	. spectra	in CDCl <sub>3</sub>						

Aryl group	v(s NH <sup>A</sup>	str) (cm NH <sup>B</sup>	<sup>-1</sup> ) CO	λ <sub>max</sub> (nm) <sup>c</sup>	Me <sup>D</sup>	Aromatic <sup>E</sup>	<sup>1</sup> H n.m.r. (δ) CH= <sup>F</sup>	NH <sup>A,D</sup>	NH <sup>B,G</sup>
Phenyl	3400 <sup>H</sup> 3440 <sup>I</sup>	3160 <sup>н</sup> 3160 <sup>1</sup>	1670 <sup>н</sup> 1675 <sup>1</sup>	$\begin{array}{c} 245 \ (3 \cdot 68) \\ 296 \ (3 \cdot 97) \\ 312 \ (3 \cdot 99) \\ 369 \ (4 \cdot 25) \end{array}$	2.21	7.05-7.45	7 80-8 00	9.90	11 · 50
2-Chlorophenyl	3380 <sup>н</sup> 3440 <sup>1</sup>	3140 <sup>H</sup> 3160 <sup>1</sup>	1660 <sup>н</sup> 1680 <sup>1</sup>	$\begin{array}{c} 309 \ (4 \ 29) \\ 245 \ (3 \cdot 81) \\ 299 \ (3 \cdot 99) \\ 319 \ (3 \cdot 98) \\ 372 \ (4 \cdot 22) \end{array}$	2.22	7 • 10-7 • 55	8.05-8.25	10.05	11.80
3-Chlorophenyl	3400 <sup>н</sup> 3440 <sup>1</sup>	3140 <sup>H</sup> 3180 <sup>I</sup>	1670 <sup>н</sup> 1680 <sup>1</sup>	$\begin{array}{c} 245 & (3 \cdot 83) \\ 298 & (4 \cdot 02) \\ 316 & (4 \cdot 01) \\ 369 & (4 \cdot 23) \end{array}$	2.20	7 · 10–7 · 30	7 • 808 • 00	10.00	11.50
4-Chlorophenyl	3380 <sup>н</sup> 3440 <sup>1</sup>	3160 <sup>н</sup> 3170 <sup>1</sup>	1670 <sup>н</sup> 1680 <sup>ı</sup>	$\begin{array}{c} 245 & (3 \cdot 70) \\ 300 & (4 \cdot 03) \\ 320 & (4 \cdot 00) \\ 373 & (4 \cdot 26) \end{array}$	2.20	7 • 20–7 • 40	7 • 82 - 8 • 02	9.82	11·40

<sup>A</sup> Ring. <sup>B</sup> Exocyclic. <sup>C</sup> log  $\varepsilon$  values in parentheses. <sup>D</sup> Singlet. <sup>E</sup> Multiplet. <sup>F</sup> Doublet. <sup>G</sup> Broad unresolved signal due to poor solubility of the compounds in CDCl<sub>3</sub>. <sup>H</sup> KBr disc. <sup>I</sup> In CHCl<sub>3</sub>.

If structure (20;  $\mathbf{R} = \mathbf{H}$ ) is the dominant tautomeric form of 5-methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one its ultraviolet absorption spectrum should be similar to that of the dimethyl derivative 1,2,5-trimethyl-4-[(phenylimino)methyl]-1,2-dihydro-3*H*-pyrazol-3-one (30) of fixed structure which contains the same group of chromophores. Compound (30), which is a new compound, was therefore synthesized. It was prepared by reaction of 1,2,5-trimethyl-3-oxo-2,3-dihydro-1*H*pyrazole-4-carbaldehyde (31) with aniline. The aldehyde (31) was synthesized by a Vilsmeier formylation of 1,2,5-trimethyl-1,2-dihydro-3*H*-pyrazol-3-one (32)<sup>40</sup> by a

<sup>40</sup> Wiley, R. H., and Wiley, P., 'Pyrazolones, Pyrazolidones and Derivatives' p. 246 (Interscience: New York 1964).

route analogous to the preparation of 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbaldehyde from 1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (antipyrine).<sup>41,42</sup>

1,2,5-Trimethyl-4-[(phenylimino)methyl]-1,2-dihydro-3*H*-pyrazol-3-one (30) shows two ultraviolet absorption bands at 242 and 329 nm (log  $\varepsilon$  3.96 and 4.23) whereas 5-methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one shows four absorption bands at 245, 296, 312 and 369 nm (log  $\varepsilon$  3.68, 3.97, 3.99 and 4.25). The two absorption spectra are quite different. It is evident, therefore, that 5-methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one does not exist in the tautomeric form (20;  $\mathbf{R} = \mathbf{H}$ ). It must, therefore, exist as the (phenylamino)methylene structure (18;  $\mathbf{R} = \mathbf{H}$ ).

Representation of the structure of 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones in the tautomeric form (18; R = H) is in full accord with the spectroscopic data in Table 2. The infrared spectra of 5-methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one and its *o*-, *m* and *p*-chlorophenyl analogues in the solid state and in solution showed absorption maxima at 1660–1675, 3140–3180 and 3380–3440 cm<sup>-1</sup> which were assigned to CO, NH (exocyclic) and NH (ring) stretching frequencies respectively. The NH frequency assigned to the exocyclic NH at 3140–3180 cm<sup>-1</sup> is low for an unbonded NH group and since the frequency was independent of the concentration of the solution it is inferred that the exocyclic NH group is involved in intramolecular hydrogen bonding. The ultraviolet spectra show a strong maxima at about 370 nm in accord with the presence of conjugated chromophores in structure (18; R = H). The n.m.r. spectra were consistent with structure (18; R = H). In addition to absorptions assigned to methyl, methine, aromatic and ring NH protons a broad absorption at about  $\delta$  11 · 5 was present which is attributable to the intramolecular bonded NH proton.

Corroborative evidence that 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*pyrazol-3-ones exist in the tautomeric form (18; R = H) comes from comparison of their spectra (Table 2) with the spectra of the corresponding 2,5-dimethyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones (18; R = Me) (Table 3). The 2,5-dimethyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones were prepared by reaction of 2,5-dimethyl-2,4-dihydro-3*H*-pyrazol-3-one with the appropriate *N*,*N'*diarylmethanimidamide. A co-product obtained from the reaction consisted of 4-[(5-hydroxy-1,3-dimethyl-1*H*-pyrazol-4-yl)methylene]-2,5-dimethyl-2,4-dihydro-3*H*pyrazol-3-one (33)<sup>43,44</sup> the identity of which was fully established by comparison of its infrared spectrum with that of the published spectrum.<sup>45</sup>

The infrared spectra of 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones and 2,5-dimethyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones both show absorption maxima at 1660–1670 and 3160–3230 cm<sup>-1</sup> due to CO and NH (exocyclic) stretching frequencies respectively. The ultraviolet spectra of the two series of compounds show four absorption bands at similar wavelengths while the n.m.r. spectra in both series show signals at almost identical chemical shifts for the

42 Ledrut, J., Winternitz, F., and Combes, G., Bull. Soc. Chim. Fr., 1961, 704.

<sup>44</sup> Haensel, W., Justus Liebigs Ann. Chem., 1976, 1680.

<sup>&</sup>lt;sup>41</sup> Ito, I., J. Pharm. Soc. Jpn, 1956, 76, 167 (Chem. Abstr., 1956, 50, 13939).

<sup>&</sup>lt;sup>43</sup> Porai-Koshits, B. A., Kvitko, I. Y., and Shutkova, E. A., Khim.-Farm. Zh., 1970, 4, 19 (Chem. Abstr., 1970, 73, 3844).

<sup>&</sup>lt;sup>45</sup> Bratan-Mayer, S., Strohbusch, F., and Haensel, W., Z. Naturforsch., Teil B, 1976, 31, 1106.

*C*-methyl, aromatic, methine and exocyclic NH protons. Since the 2,5-dimethyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones have already been deduced to exist as the (arylamino)methylene tautomer (18; R = Me)<sup>31,32</sup> the similarity in the two series of spectra confirms that the 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones also exist as the (arylamino)methylene tautomer (18; R = H).

Overall the evidence is overwhelming that the 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones exist as the (arylamino)methylene tautomer (18; R = H) with intramolecular hydrogen bonding between the CO and exocyclic NH groups.

Table	3.	Spectra	of	2,5-dimethyl-4-[(arylamino)methylene]-2,4-dihydro-3H-pyrazol-3-ones	(18;
				$\mathbf{R} = \mathbf{M}\mathbf{e}$ )	

Aryl group	$v(str) (cm^{-1})$ NH CO		$\lambda_{\max}$ (nm)	CMe <sup>A</sup>	Aromatic	<sup>1</sup> H n.m.r. $(\delta)$ CH= <sup>B</sup>	NMe <sup>A</sup>	NH <sup>B</sup>	
Phenyl	3230	1670	242 $(3 \cdot 77)$ 295 $(4 \cdot 00)^{c}$ 322 $(4 \cdot 19)$ 366 $(4 \cdot 17)$	2.25	7 • 15–7 • 60	7.85-8.05	3 • 42	11 • 25-11 • 45	
2-Chlorophenyl	3220	1665	$242 (3 \cdot 82) 300 (4 \cdot 02) 328 (4 \cdot 21) 366 (4 \cdot 14)$	2.26	7 • 20 – 7 • 60	7.90-8.10	3 · 42	11 • 75–11 • 95	
3-Chlorophenyl	3230	1670	$\begin{array}{c} 241 & (3 \cdot 78) \\ 300 & (4 \cdot 03)^{c} \\ 324 & (4 \cdot 20) \\ 364 & (4 \cdot 12) \end{array}$	2.25	7 • 15–7 • 40	7.80-8.00	3 · 45	11 • 20–11 • 40	
4-Chlorophenyl	3230	1665	240 (3 · 70) 314 (4 · 08) <sup>c</sup> 328 (4 · 20) 368 (4 · 18)	2.25	7 • 10–7 • 50	7.80-8.00	3.45	11 • 25 - 11 • 45	

I.r. and u.v. spectra were run in CHCl<sub>3</sub>; n.m.r. in CDCl<sub>3</sub>

<sup>A</sup> Singlet. <sup>B</sup> Doublet. <sup>C</sup> Shoulder.

## Experimental

Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Light petroleum had b.p. 60-80°. N.m.r. spectra (60 MHz) were determined by using tetramethylsilane as the internal standard.

#### 5-Methyl-4-[(arylamino)methylene]-2,4-dihydro-3H-pyrazol-3-ones (18; R = H) (Tables 1 and 2)

5-Methyl-2,4-dihydro-3*H*-pyrazol-3-one (0.025 mol) and the appropriate *N*,*N'*-diarylmethanimidamide (0.025 mol) were heated together at 170–180° for 20 min. The mixture was cooled and dilute aqueous hydrochloric acid (*c*. 26 ml) was added to neutralize the arylamine formed in the reaction. The solid product was collected and recrystallized from ethanol to afford the 5-methyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one in 40–60% yield.

#### 1,2,5-Trimethyl-3-oxo-2,3-dihydro-1H-pyrazole-4-carbaldehyde (31)

Dimethylformamide (0.04 mol) was dissolved in a mixture of chloroform (5 ml) and toluene (5 ml) in a three-necked flask fitted with thermometer, stirrer and dropping funnel. To the latter was attached a calcium chloride guard tube. The mixture was cooled to 0° and phosphorus oxychloride (0.043 mol) was added dropwise at such a rate as to maintain the low temperature. A

solution of 1,2,5-trimethyl-1,2-dihydro-3*H*-pyrazol-3-one<sup>40</sup> (0.04 mol) in chloroform (5 ml) was added slowly. After the addition, the reaction mixture was allowed to come to ambient temperature and was then heated at 60-65° for 3 h. The mixture was left overnight and then decomposed by iced water. The solution was neutralized with sodium bicarbonate to pH 7.0. The solvents were removed under vacuum and the remaining solid was extracted with hot chloroform. After drying (MgSO<sub>4</sub>), the solvent was removed to afford a solid which was crystallized from tetrahydrofuran to afford 1,2,5-trimethyl-3-oxo-2,3-dihydro-1H-pyrazole-4-carbaldehyde as white crystals, m.p. 203–204° (yield 40%) (Found: C, 54.85; H, 6.65; N, 17.9. C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires C, 54.55; H, 6.5; N, 18.2%). N.m.r.  $\delta$  (CDCl<sub>3</sub>) 2.56, s, 3H, CCH<sub>3</sub>; 3.44, s, 3H, NCH<sub>3</sub>; 3.56, s, 3H, NCH<sub>3</sub>; 9.86, s, 1H, CHO. U.v.  $\lambda_{max}$  (EtOH) 224 nm (log e 4.08), 296 (3.97). This compound is reported in the index of *Chemical Abstracts* but the original paper contains no reference to the compound.<sup>46</sup>

#### 1,2,5-Trimethyl-4-[(phenylimino)methyl]-1,2-dihydro-3H-pyrazol-3-one (30)

1,2,5-Trimethyl-3-oxo-2,3-dihydro-1*H*-pyrazole-4-carbaldehyde (0.0013 mol) was mixed with freshly distilled aniline and the mixture heated to 120° for 5 min. The mixture was cooled and the solid was crystallized from tetrahydrofuran to afford 1,2,5-trimethyl-4-[(phenylimino)methyl]-1,2-dihydro-3H-pyrazol-3-one as white crystals, m.p. 175° (yield 75%) (Found: C, 67.95; H, 6.7; N, 18.0. C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O requires C, 68.1; H, 6.55; N, 18.2%). N.m.r.  $\delta$  (CDCl<sub>3</sub>) 2.68, s, 3H, CCH<sub>3</sub>; 3.42, s, 3H, NCH<sub>3</sub>; 3.45, s, 3H, NCH<sub>3</sub>; 7.10-7.40, m, 5H, aromatic; 8.48, s, 1H, CH=N. U.v.  $\lambda_{max}$  (CHCl<sub>3</sub>) 242 nm (log  $\varepsilon$  3.96), 252sh (3.93), 329 (4.23). I.r.  $v_{max}$  (KBr, CHCl<sub>3</sub>) 1640 cm<sup>-1</sup> (CO).

#### 2,5-Dimethyl-4-[(arylamino)methylene]-2,4-dihydro-3H-pyrazol-3-ones (18; R = Me) (Table 3)

2,5-Dimethyl-2,4-dihydro-3*H*-pyrazol-3-one (0.009 mol) and excess of the appropriate N,N'-diarylmethanimidamide (0.016 mol) were ground together and heated at 80–120° for 5 min. The reaction mixture was cooled and neutralized with dilute aqueous hydrochloric acid. The orange solid which precipitated was collected, washed with water, dried and crystallized from chloroform to afford 4-[(5-hydroxy-1,3-dimethyl-1*H*-pyrazol-4-yl)methylene]-2,5-dimethyl-2,4-dihydro-3*H*-pyrazol-3-one (33) (c. 0.4 g), m.p. 212°. The literature melting points are 214°<sup>43</sup> and 217°.<sup>44</sup> The infrared spectrum was identical to the published spectrum.<sup>45</sup> The mother liquors and washings were allowed to stand for a few days whereupon a thick yellow precipitate was produced. The solid was collected and crystallized to afford the 2,5-dimethyl-4-[(arylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones in 20–26% yield.

Details of the compounds are as follows. The spectra are recorded in Table 3.

2,5-Dimethyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one was crystallized from light petroleum. It had m.p.  $154^{\circ}$  (lit.<sup>32,43</sup> 156–157°).

2,5-Dimethyl-4-[(2-chlorophenylamino)methylene]-2,4-dihydro-3H-pyrazol-3-one had m.p.  $158^{\circ}$  (from light petroleum/ethyl acetate) (Found: C, 57.4; H, 5.1; N, 16.7.  $C_{12}H_{12}ClN_3O$  requires C, 57.7; H, 4.8; N, 16.8%).

2,5-Dimethyl-4-[(3-chlorophenylamino)methylene]-2,4-dihydro-3H-pyrazol-3-one had m.p. 108° (from ethanol) (Found: C, 57·4; H, 5·1; N, 16·7%).

2,5-Dimethyl-4-[(4-chlorophenylamino)methylene]-2,4-dihydro-3H-pyrazol-3-one had m.p. 158–159° (from light petroleum/ethyl acetate) (Found: C, 57.7; H, 5.0; N, 16.9%).

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<sup>46</sup> Von Weissenborn, V., Brandt, H. H., and Schulte, K. E., *Arch. Pharm. (Weinheim, Ger.)*, 1977, **310**, 1018 (*Chem. Abstr.*, 1978, **88**, 152539).