

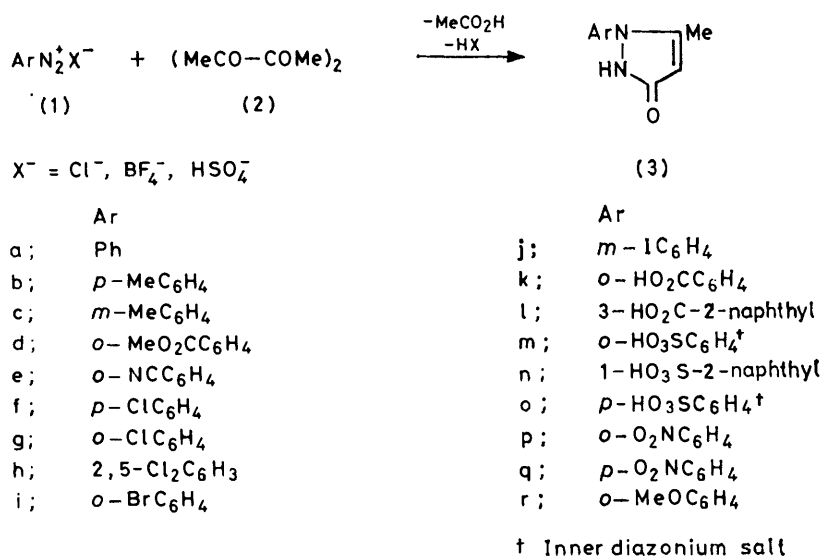
## A Novel Synthesis of Pyrazol-3-ones from Biacetyl Dimer and Arenediazonium Salts

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Arenediazonium salts (1) and biacetyl dimer (2), under acidic conditions, yield 1-aryl-5-methylpyrazol-3-ones (3). A simple procedure employing solid diazonium salts is described. Intermediate 2-arylaazo-2,5-dimethylfuran-3(2H)-ones (7) are involved in the reaction. In acid media they can be converted into the pyrazolones (3). Their formation is discussed. A possible mechanism for the rearrangement of (7) to (3) is suggested.

1-ARYL-5-METHYLPYRAZOL-3-ONES (3) are generally prepared by condensation of  $\beta$ -acylarylhiazines and acetoacetic ester with phosphorus trichloride or oxychloride,<sup>1</sup> or from diketene and arylhydrazines.<sup>2</sup> We now report a novel synthesis of the pyrazolones (3) from

acidic conditions for the formation of (3) could be obtained. The latter method appeared to be more convenient (higher yields, purer products) and, therefore, was applied to the synthesis of 1-aryl-5-methylpyrazol-3-ones (3). To obtain relatively stable solid diazonium



SCHEME 1

the arenediazonium salts (1) and biacetyl dimer (2)<sup>3</sup> (Scheme 1). We have previously described<sup>4</sup> the synthesis of Michaelis' benzopyrazolopyrazolodione (5)<sup>5</sup> and the pyrazol-3-one (3d) (30 and 49% yield, respectively) simply by treating aqueous solutions of the diazotized amines (1k) and (1d) ( $\text{X}^- = \text{Cl}^-$ ) respectively with (2). Compound (5) was shown to be formed by cyclisation of the intermediate pyrazol-3-one (4a). Our attempts to extend the synthesis of (3), under similar conditions (pH 0.4–0.5),<sup>†</sup> to other aromatic amines were unsuccessful. Thus, except for *p*- and *o*-nitroaniline (55 and 30% yield, respectively), the corresponding pyrazol-3-ones were obtained in less than 5% yield. By carrying out the reaction in 5M-hydrochloric acid or employing diazonium salts (1) in the solid state, suitable

salts, fluoroborate or chloride as anion (for amines easily diazotizable in water or in alcohol by sodium or alkyl nitrite, respectively) and hydrogen sulphate (for poorly basic amines diazotisable by nitrosylsulphuric acid) were chosen. Reaction took place simply by keeping the stirred mixture of the reactants at 40–45 °C for 5 h. Generally a lower temperature (20–30 °C) gave less good results and some unchanged diazonium salt was recovered. A 2 : 1 biacetyl dimer : diazotized amine molar ratio was normally used. In some cases, to favour the mixing of the reactants or to avoid an over fast reaction with formation of tars, dimethoxyethane was added to the mixture. The products resulted as the salts of (3).<sup>1c</sup> When the anion of (1) was chloride the

<sup>†</sup> Final pH of the mixture was *ca.* 0.

<sup>1</sup> (a) F. Stolz, *J. prakt. Chem.*, 1897, **55**, 150; (b) K. Mayer, *Ber.*, 1903, **36**, 717; (c) A. Michaelis, *Annalen*, 1905, **338**, 267.

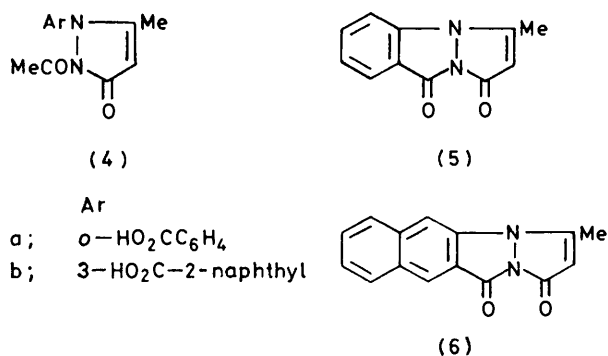
<sup>2</sup> H. Z. Lecher, R. P. Parker, and R. C. Conn, *J. Amer. Chem. Soc.*, 1944, **66**, 1959.

<sup>3</sup> (a) O. Diels, W. M. Blanchard, and H. V. d'Heyden, *Ber.*, 1914, **47**, 2355; (b) A. J. Birch and C. J. Maye, *J. Chem. Soc.*, 1957, 412.

<sup>4</sup> C. Venturello and G. P. Chiusoli, *Chem. and Ind.*, 1971, 1415.

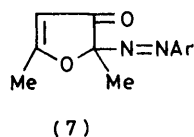
<sup>5</sup> (a) A. Michaelis, *Annalen*, 1910, **373**, 148, 202; (b) S. Veibel and H. Lillelund, *Tetrahedron*, 1957, **1**, 201.

hydrochlorides were easily isolated from the reaction mixture. Of the examined diazonium salts *p*-hydroxybenzenediazonium chloride failed to give the corresponding pyrazol-3-one. In the case of the *ortho*-isomer little



(5–6%) of the product, m.p. 186–188 °C (hot water), with analytical and spectral data consistent with the pyrazol-3-one structure was isolated. The results are summarized in Table 1.

It was found that under certain conditions (aqueous experiments, pH 0.4–0.5) the intermediate yellow furanones (7) could be isolated which, on treatment with concentrated hydrochloric acid, rearranged to (3). The ease of this rearrangement was found to be strongly dependent on the acidity of the reaction medium and, moreover, to vary according to the nature of the aryl substituents. The formation of (3) appears to be favoured by the presence of electron-attracting substituents and disfavoured by the presence of electron-donating substituents. Thus, (7d) proved reactive (100 °C) even at pH *ca.* 2 (glacial acetic acid–water 1.3 : 1 v/v). The formation of the intermediate furanones (7) in aqueous solution is very likely to occur *via*



Ar	Ar
a; Ph	d; <i>o</i> -MeO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>
b; <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	e; <i>o</i> -NCC <sub>6</sub> H <sub>4</sub>
c; <i>m</i> -MeC <sub>6</sub> H <sub>4</sub>	f; <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>

initial transformation of the biacetyl dimer [behaving as (8)<sup>3b</sup> instead of as (9)] into 2,5-dimethylfuran-3(2*H*)-one (12), followed by a coupling reaction between the latter [probably in the enol form (11)] and the diazonium salt (1) (Scheme 2). This pathway is supported by the fact that both steps have been observed.

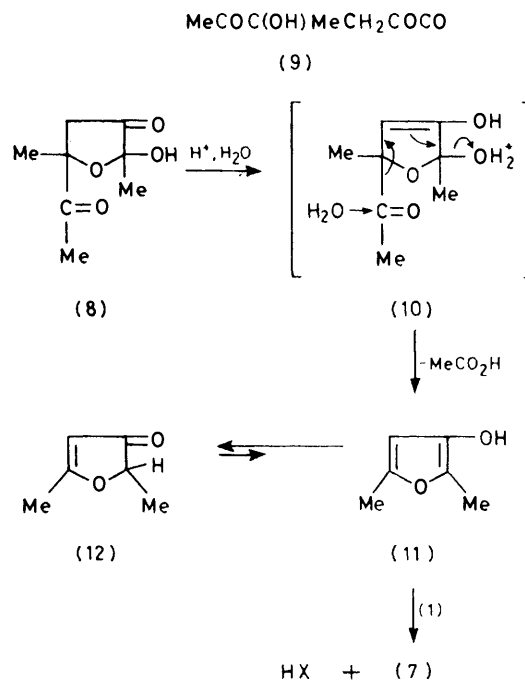
<sup>6</sup> R. E. Rosenkranz, K. Allner, R. Good, W. v. Philipsborn, and C. H. Eugster, *Helv. Chim. Acta*, 1963, **46**, 1259.

<sup>7</sup> D. de Rijke, *Fr.P.* 2,211,457/1974.

<sup>8</sup> I. I. Nazarova, G. P. Gusev, V. F. Kucherov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 1580 (*Chem. Abs.*, 1968, **68**, 2549p).

In aqueous solution (pH 0.3–0.4) the biacetyl dimer was found, indeed, to give rise to 2,5-dimethylfuran-3(2*H*)-one (12) which was identical with an authentic sample.<sup>6–8</sup> By addition of (12) to the acidified aqueous solution (pH 0.2–0.3) of the diazonium salts (1a–f) the corresponding furanones (7a–f) were formed. The coupling conditions of (12) agree with those reported for benzofuran-3(2*H*)-one systems.

The same sequence of reactions [(2) → (12) → (7)] is likely when using diazonium salts.<sup>9</sup> Thus, biacetyl dimer warmed at 40–50 °C in the presence of a strongly



SCHEME 2

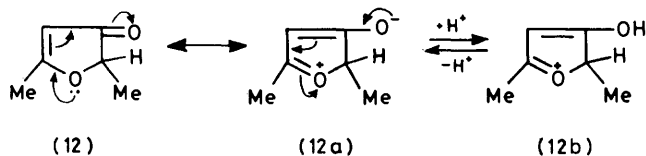
acid cation-exchanger gave (12). Yet (12) reacted with solid diazonium salts to afford directly the corresponding pyrazolones (3). In this case, presumably, the diazonium salt itself provides the necessary acidity to promote the transformation of (2) into (12). It should be emphasized that the formation, in acid medium, of 2,5-dimethylfuran-3-one from biacetyl dimer, although already postulated by some authors,<sup>10</sup> has not before been observed. Presumably it involves the intermediate (10) from which, by hydrolytic cleavage of the acetyl group with simultaneous loss of water, (12) may be formed.

2-Arylazo-2,5-dimethylfuran-3(2*H*)-ones (7) appear to be less stable to mineral acids than 2,5-dimethylfuran-3(2*H*)-one (12). Rosenkranz *et al.*<sup>6</sup> attribute the acid stability of the latter to its behaviour as a vinylogous lactone rather than as an enol ether. This would involve a high contribution of the structure (12a) to the

<sup>9</sup> A. R. Katritzky and J. M. Lagowski, 'The Principles of Heterocyclic Chemistry,' Methuen, London, 1967, p. 129

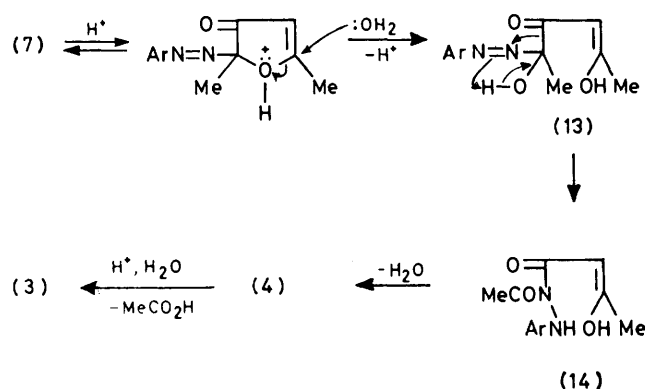
<sup>10</sup> R. Shapiro, J. Hachmann, and R. Wahl, *J. Org. Chem.*, 1966, **31**, 2710.

ground state of the molecule and protonation at the C-3 oxygen (12b) would be preferentially expected. The electronic influence of the arylazo-group might result in



a reduction (the degree depending on the nature of the substituents on the aryl ring) of the contribution of such a structure to the ground state of (7) and so favour the protonation at the ethereal oxygen.

Accordingly a reasonable mechanism for the rearrangement of (7) to (3) might be the one presented in Scheme 3. Acetoacetic arylhydrazide has long been



SCHEME 3

postulated as the reactive precursor of (3)<sup>1c,2</sup> and the formation of (4) in the final step is supported by the isolation of compounds (4a and b) when the reaction was carried out in aqueous solution (pH 0.4–0.5). Attempts to prove the suggested mechanism are in progress.

#### EXPERIMENTAL

I.r., u.v., <sup>1</sup>H n.m.r., and mass spectra were recorded on the following instruments: a Perkin-Elmer 125, a Unicam SP 1800, a Bruker WH-90, and a Varian MAT CH 5. T.l.c. was performed on Merck silica gel (5719) and the products were detected by using a u.v. lamp. Column chromatography was performed on Merck silica gel 60 (7 734). Self-condensation of biacetyl was carried out by a known procedure.<sup>3</sup> The oily fraction b.p. 95–102 °C at 0.2 mmHg, was used.

**Preparation of Solid Arenediazonium Salts (1).**—Diazonium fluoroborates<sup>11,12a</sup> and chlorides<sup>13</sup> were prepared by standard procedures. To prepare 3-carboxynaphthalene-2-diazonium chloride (11), the volume of alcohol used as solvent was double that described. Diazonium hydrogen sulphates were prepared by the Hodgson-Mehadavan

\* Handling of benzenediazonium-*p*-sulphonic acid (10) when dry or nearly so is to be avoided since it readily explodes.

<sup>11</sup> A. Roe, *Org. Reactions*, 1949, **5**, 193.

<sup>12</sup> A. Vogel, 'Practical Organic Chemistry,' Longmans, London, 2nd edn., (a) p. 584–587; (b) p. 596.

method<sup>14</sup> (1c and h) or by using a solution of solid nitrosyl-sulphuric acid<sup>15a</sup> in acetic<sup>15a</sup> or 78% sulphuric acid<sup>15b</sup> (1e, j, and p). Arenediazonium sulphonic acids (inner salts) were prepared by the inverted method.<sup>12b</sup> The salts precipitated from the aqueous solution were filtered off, washed with ice-water (minimum amount) and acetone and then dried.\* In the diazotization of aniline-*o*-sulphonic acid water was reduced to one fifth of the stated volume.

**1-Aryl-5-methylpyrazol-3-ones (3).**—*General procedure.* A stirred mixture of solid diazonium salt (1) (8.7 mmol) and biacetyl dimer (17.4 mmol) [with addition, if necessary, of dimethoxyethane (3 ml)] was kept at 40–45 [50–60] °C for 5 h. 30% Sodium hydroxide was added to the mixture and organic matter was extracted with ether and chloroform. Addition of 10% hydrochloric acid to the aqueous solution precipitated the product that was filtered off, washed with water, and dried. It was purified, if necessary, by refluxing the corresponding hydrochloride (obtained from an alcoholic solution of pyrazolone and 10% hydrochloric acid) in acetone.

When arenediazonium sulphonic acids or chlorides were used, the product directly separated (as the hydrochloride in the latter case) from the reaction mixture on addition of ether. It was filtered off, washed, and then refluxed in acetone (washed again, in the former case, with a little ice-water and acetone) and dried. The pyrazolone was obtained from the hydrochloride in the usual manner. To isolate (3d) treatment with sodium hydroxide was avoided. The mixture was dissolved in chloroform and the organic layer was washed with water and evaporated. On addition of ether to the residue the product separated, and this was filtered off, washed (ether), and dried. The chemical and spectral properties of (3) were consistent with the assigned structure. They coupled with diazotized aromatic amines to give dyes similar to those obtained from 1-aryl-3-methylpyrazol-5-ones. The solid-state i.r. spectra exhibited the absence of a normal carbonyl band and the presence of a strong absorption at 3 100–2 300 cm<sup>-1</sup> indicating strong hydrogen bonding.<sup>16</sup>

**2-Acetyl-1-(*o*-carboxyphenyl)-5-methylpyrazol-3-one (4a).**—Anthranilic acid (1.19 g, 8.7 mmol) dissolved in water (1.8 ml) and concentrated hydrochloric acid (1.8 ml) and diazotized at 0 °C with sodium nitrite (9 mmol) in water (2.5 ml) was stirred and treated at 20 °C with biacetyl dimer (5 g, 29 mmol) for 6 h. The mixture was then set aside overnight at room temperature. Addition of water to the stirred mixture precipitated the product. This was filtered off, washed with water, and dried and then washed again several times with ether and ether-acetone (1 : 1) before being dried a second time (1.24 g, 55%); the product was recrystallized from acetone (–30 °C) (Found: C, 60.2; H, 4.45; N, 11.05. C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub> requires C, 60.0; H, 4.65; N, 10.75%),  $\nu_{\max}$  (Nujol) 1 728, 1 716, 1 632 (1 728br and 1 693br in CHCl<sub>3</sub>), 1 261, and 1 251 cm<sup>-1</sup>;  $\delta$  [<sup>2</sup>H<sub>5</sub>]pyridine) 2.0 (3 H, d, *J* 0.8 Hz, 5-Me), 2.55 (3 H, s, MeCO), 5.5 (1 H, q, *J* 0.8 Hz, 4-H), 7.19–7.60 (3 H, m, ArH), 7.97–8.18 (1 H, m, ArH), and 11.77br (1 H, s, exch. CO<sub>2</sub>H); *m/e* 260 (*M*<sup>+</sup>) 218 and 200. Above 155 °C

<sup>13</sup> M. Stiles, R. G. Miller, and U. Burckhardt, *J. Amer. Chem. Soc.*, 1963, **85**, 1792; see also E. Knoevenagel, *Ber.*, 1895, **28**, 2048; B. Hirsch, *ibid.*, 1897, **30**, 1148.

<sup>14</sup> H. Hodgson and A. P. Mahadevan, *J. Chem. Soc.*, 1947, 325.

<sup>15</sup> (a) M. R. Piercey and E. R. Ward, *J. Chem. Soc.*, 1962, 3841; (b) K. Schnitzspahn, *P. Friedlaender's Fortschritte der Teerfarbenfabrikation*, 1934, **21**, 967.

<sup>16</sup> A. R. Katritzky and F. W. Maine, *Tetrahedron*, 1964, **20**, 315.

it was converted without melting (loss of acetic acid) into 3-methylbenzo[*c*]pyrazolo[1,2-*a*]pyrazole-1,9-dione (5). The structure of (4a) was proved chemically by *X*-ray methods.<sup>4</sup>

TABLE 1

1-Aryl-5-methylpyrazol-3-ones (3) prepared from biacetyl dimer (2) and solid arenediazonium salts (1)

Product † (3)	Yield <sup>a</sup> (%)	X	M.p. (°C) <sup>b</sup>
a <sup>c</sup>	45	BF <sub>4</sub>	168—170 <sup>d</sup>
b <sup>c</sup>	66	BF <sub>4</sub>	196 <sup>e</sup>
c <sup>c</sup>	30 <sup>f,g</sup>	HSO <sub>4</sub>	170—171
d	60	BF <sub>4</sub>	163—164 <sup>h</sup>
e	61	HSO <sub>4</sub>	182—184
f	70	Cl	228—230 <sup>i</sup>
g	70	Cl	187—189 <sup>j</sup>
h <sup>c</sup>	65 <sup>f,g</sup>	HSO <sub>4</sub>	245—248 <sup>k</sup>
i	60 <sup>f</sup>	Cl	209—210 <sup>l</sup>
j <sup>m</sup>	64 <sup>f</sup>	HSO <sub>4</sub>	221—223
k	60	Cl	228—232 <sup>n</sup>
l	69	Cl	<sup>o</sup>
m	80	Inner salt	dk. > 300 <sup>p</sup>
n	81	Inner salt	dk. > 300 <sup>p,q</sup>
o	87	Inner salt	dk. > 300 <sup>r</sup>
p <sup>c</sup>	70	HSO <sub>4</sub>	218—220
q	80	BF <sub>4</sub>	265—268 <sup>s</sup> (dec.)
r <sup>c</sup>	42	BF <sub>4</sub>	186—187

dk. = darkens.

† For analytical data see Supplementary Publication.

<sup>a</sup> Before recrystallization. <sup>b</sup> From 95% ethanol; m.p.s uncorrected (determined with a Kofler hot-stage apparatus). <sup>c</sup> Purified as the hydrochloride. <sup>d</sup> Lit.,<sup>16</sup> m.p. 171—173.5 °C; labile from m.p. 157—159 °C (lit.<sup>1c</sup> m.p. 157 °C). <sup>e</sup> Lit.<sup>1c</sup> m.p. 196 °C. <sup>f</sup> Addition of dimethoxyethane. <sup>g</sup> 26.1 Mmole of biacetyl dimer were used. <sup>h</sup> Lit.<sup>5b</sup> m.p. 163—164 °C. <sup>i</sup> Lit. m.p. 219—221 °C (Y. Usui and C. Matsumura, *Yakugaku Zasshi*, 1967, **87**, 38). <sup>j</sup> Lit. m.p. 183—185 °C (cf. footnote <sup>i</sup>). <sup>k</sup> Lit.<sup>2</sup> m.p. 245—248 °C. <sup>l</sup> Usually melts at 201—203 °C, resolidifies and remelts at 209—210 °C. <sup>m</sup> The sparingly soluble sodium salt was filtered off, refluxed in acetone, dissolved in water, and acidified. <sup>n</sup> Lit.<sup>5b</sup> m.p. 232—234 °C. Above m.p. it cyclises to (5). <sup>o</sup> Above 230 °C cyclises to (6) without melting. <sup>p</sup> From water-methanol. <sup>q</sup> Monohydrate; anhydrous at 250 °C. <sup>r</sup> From water. <sup>s</sup> Lit. m.p. > 260 °C (M. A. de Ramaix and J. Jaeken, *Belg.P.* 563,474/1958).

**2-Acetyl-1-(3-carboxy-2-naphthyl)-5-methylpyrazol-3-one** (4b).—This compound was prepared and isolated as above from solid 3-carboxynaphthalene-2-diazonium chloride (2.04 g, 8.7 mmol) dissolved in cold water (5 ml) and concentrated hydrochloric acid (0.3 ml); the yield was 1.48 g (55%). It was recrystallized from acetone (−30 °C) (Found: C, 65.55; H, 4.35; N, 8.85. C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub> requires C, 65.80; H, 4.55; N, 9.03%),  $\nu_{\max}$  (Nujol) 1728, 1712, 1647, 1733 (1727br and 1792br in CHCl<sub>3</sub>), 1244, and 1220 cm<sup>−1</sup>;  $\delta$ (<sup>2</sup>H<sub>5</sub>)pyridine 2.08 (3 H, d, *J* 0.8 Hz, 5-Me), 2.63 (3 H, s, MeCO), 5.61 (1 H, q, *J* 0.8 Hz, 4-H), 7.23—7.63 (2 H, m, ArH), 7.63—8.13 (2 H, m, ArH), 8br (1 H, s, ArH), 8.72br (1 H, s, ArH), and 10.03br (1 H, s, exch., CO<sub>2</sub>H); *m/e* 310 (*M*<sup>+</sup>), 268, 250. Above 160 °C it was converted without melting (loss of acetic acid) into 3-methylnaphtho[2,3-*c*]pyrazolo[1,2-*a*]pyrazole-1,11-dione (6).

**3-Methylnaphtho[2,3-*c*]pyrazolo[1,2-*a*]pyrazole-1,11-dione** (6).—Phosphorus trichloride (1.8 ml, 20 mmol) was added dropwise, with cooling, to the pyrazolones (3l) or (4b). The mixture, heated slightly in order to start the reaction,

\* Sparingly soluble.

† For details of the Supplementary Publications scheme, see *J.C.S. Perkin I*, 1977, Index issue, Notices to Authors, No. 7.

was set aside at room temperature for 5—10 min and then heated on a steam-bath for 1/2 h. Water (20 ml) was then added in small quantities to the mixture. The yellow product was filtered off, washed several times with water, and dried; yield 80—90%. Recrystallized from glacial acetic acid it had m.p. >310 °C (decomp.) (Found: C, 72.05; H, 4.2; N, 11.2. C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires C, 72.0; H, 4.05; N, 11.2%),  $\nu_{\max}$  (Nujol) 1746, 1670, and 1632 cm<sup>−1</sup>;  $\delta$ (CDCl<sub>3</sub>) \* 2.56 (3 H, d, *J* ca. 1 Hz, 3-Me), 5.29 (1 H, q, *J* ca. 1 Hz, 2-H), 7.20—7.84 (4 H, m, ArH), 7.36br (1 H, s, ArH), and 8.29br (1 H, s, ArH); *m/e* 250 (*M*<sup>+</sup>). A dilute solution of (6) in glacial acetic acid or ethanol showed a green fluorescence. By treatment of (6) with 30% sodium hydroxide the yellow colour disappeared. Upon addition in the cold of dilute hydrochloric acid the acid (3 l) was precipitated.

**2-Arylazo-2,5-dimethylfuran-3(2H)-ones** (7).—*Method A.* (i) The amine (20 mmol) dissolved in water (4 ml) and concentrated hydrochloric acid (4 ml) and diazotised at 0 °C with sodium nitrite (20 mmol) in water (8 ml) (1a, b, and d) or (ii) the solid diazonium salt (20 mmol) (1c, e, and f) dissolved in water (12 ml) and concentrated hydrochloric acid (0.7 ml) were kept with biacetyl dimer (8 g, 46.4 mmol) for 24 h at 20—25 °C. The mixture was extracted with chloroform. The organic layer was washed with water and evaporated. The residue was separated on a silica-gel column [n-hexane-ether (or acetone): 7:3] to give the product as a yellow oil (7a, c, and d) or solid (7b, e, and f); the yields were rather low. In the most favoured cases (6a, b) it was ca. 40%.

*Method B.* (i) The amine (20 mmol) diazotised as above (1a, b, and d) or (ii) the solid diazonium salt (20 mmol) (1c, e, and f) both dissolved in cold water (50 ml) was acidified with concentrated hydrochloric acid (2 ml). 2,5-Dimethylfuran-3-one (12) (20 mmol) was added and the mixture, with stirring, was kept for 1 h at room temperature. The product, if solid, was filtered off, washed many times with water, and dried; if oily, it was extracted with ether from the solution and dried (Na<sub>2</sub>SO<sub>4</sub>). After removal of the solvent, it was further purified by column chromatography [n-hexane-ether (7:3)]; the yield was ca. 90%.

Typically, aniline gave 2,5-dimethyl-2-phenylazofuran-3-one (7a) as a yellow oil,  $n_D^{20}$  1.5808, *R<sub>F</sub>* 0.23 [silica; n-hexane-ether (7:3)] (Found: C, 66.4; H, 5.35; N, 12.8. C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> requires C, 66.65; H, 5.6; N, 12.95%),  $\nu_{\max}$  (CCl<sub>4</sub>) 1724 (CO) and 1606 (C=C) cm<sup>−1</sup>;  $\delta$ (CDCl<sub>3</sub>) 1.73br (3 H, s, 2-Me), 2.40 (3 H, d, *J* 0.75 Hz, 5-Me), 5.45 [1 H, q (on irradiation at  $\delta$  1.73), *J* 0.75 Hz, 4-H], 7.24—7.48 (3 H, m, ArH), 7.55—7.82 (2 H, m, ArH);  $\lambda_{\max}$  (MeOH) 275 and 311sh nm ( $\epsilon$  15 000 and 5 000);  $\lambda_{\min}$  406 nm ( $\epsilon$  297, concentration 0.16 g l<sup>−1</sup>); *m/e* 216 (*M*<sup>+</sup>), 112, 111, 105, 78, 77, and 43.

Physical, analytical, and spectroscopic data of compound (7b—f) are available as a Supplementary Publication SUP No. 22236 (4 pp.).†

**Transformation of Biacetyl Dimer into 2,5-Dimethylfuran-3-one** (12).—To biacetyl dimer (5 g) dissolved in water (5 ml), concentrated hydrochloric acid (0.3 ml) was added. The solution was warmed at 40—45 °C for 4 h. It was then carefully neutralized (pH 7) and extracted with diethyl ether (3 × 30 ml). The ethereal extract was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. By fractional distillation under reduced pressure of the residue a fraction, b.p. 67—72 °C at 12 mmHg, was collected. By further distillation this fraction gave

analytically pure 2,5-dimethylfuran-3-one (0.7 g), b.p. 67—69 °C at 12 mmHg (lit.,<sup>6</sup> 70—72 °C at 13 mmHg) (Found: C, 64.0; H, 7.3. Calc. for  $C_6H_8O_2$ : C, 64.25; H, 7.2%).

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