TABLE I

SUBSTITUTION PRODUCTS OF 3,5-DIMETHYL-1-(*N*,*N*-DIPHENYLCARBAMYL)PYRAZOLE

					Analyses					
					Carbon		Hydrogen		Nitrogen	
Reaction	Product	Molecular Formula	M.P., °C.	Yield, %	Calcd.	Found	Calcd.	Found	Calcd.	Found
Chlorination[a]	Ie[b,c]	$C_{19}H_{17}N_3Cl_4O$[d]	95–96	20	48.5	49.2	3.8	3.6	9.4	9.3[e]
Bromination[f]	Ig[g]	$C_{18}H_{16}N_3BrO$	147–148	98	58.4	58.3	4.3	4.3	11.4	11.4[h]
Iodination[i]	Ih[g]	$C_{18}H_{16}N_3IO$	167	98	51.8	51.7	3.8	3.6	10.1	10.1[j]
Nitration[k]	Ik[g,l]	$C_{18}H_{15}N_5O_5$	179–181	95	56.7	56.8	3.9	3.9	18.4	18.1
Reduction[m]	Im[n,l,o]	$C_{18}H_{20}N_5O_2$	247	20	63.9	64.3	5.9	5.4	20.7	20.1
Bromination[p]	Il[g,q]	$C_{18}H_{14}N_5BrO_5$	186–188	85	47.0	47.2	3.0	2.8	15.2	15.1[r]

[a] Run in chloroform at room temperature, with an excess of gaseous chlorine. [b] Recrystallized from chloroform. [c] The main product was a colorless oil so far unidentified. [d] Contains 1 molecule of solvent of crystallization ($CHCl_3$). [e] Calcd.: Cl, 31.9; Found: Cl, 31.4. [f] Dropwise addition of an equimolar quantity of bromine to Ib dissolved in chloroform, with continuous stirring of the mixture. [g] Recrystallized from 95% ethanol. [h] Calcd.: Br, 21.6; Found: Br, 21.2. [i] By reaction of Ib in acetic acid with equimolar quantities of potassium iodide and potassium iodate, with 30 minutes reflux. Compare S. H. Tucker, *J. Chem. Soc.*, 546 (1926). After 13 hr. reflux of Ib with free iodine in aqueous ethanol, 82% was recovered, *ca.* 0.2% Ij was isolated and only 3% Ih. Reaction of Ib with iodine monochloride in glacial acetic acid was much more rapid, 70% Ih being isolated after 30 min. reflux, together with 30% Ib. [j] Calcd.: I, 30.5; Found: I, 30.4. [k] Effected by maintaining a solution of Ib in a mixture of concentrated nitric and sulfuric acids at 0° for 24 hr. and then pouring the liquor onto an excess of ice. When the nitration mixture was maintained at steam-bath temperatures for 4 hr. prior to quenching with ice, the yield of Ik fell to 80% and work-up of the filtrate revealed the formation of tars. No tars were detected in the experiment run at 0°C. [l] This was obtained as yellow microcrystals. [m] This involved reduction of Ik suspended in anhydrous ether by amalgamated aluminum foil over a period of 23 hr. at room temperature. Unchanged Ik was recovered in 60% yield. [n] Recrystallized from aqueous acetone. [o] Physical data are for the monohydrate. [p] This refers to bromination of Ik by the same technique as was used with Ib. The same product (Il) is obtained (82% yield) by nitration of Ig. [q] Obtained as fine silken pale-green needles. [r] Calcd.: Br, 17.4; Found: Br, 17.4.

30% yield of Ic and a trace quantity (*ca.* 1%) of 1-(*N*,*N*-diphenylcarbamyl)piperidine (IIc), m.p. 110°, reported[19] m.p. 110°. (b) The following experiments were performed to emphasize the lack of reactivity of Ib. (1) A solution of 0.80 g. of 3,5-dimethyl-1-carbamylpyrazole[20] in 10.4 ml. of aniline was refluxed for 1 hr. It was then allowed to stand for 24 hr. and deposited a quantitative yield (1.06 g.) of 1,3-diphenylurea, m.p. 239°, reported[21] m.p. 238–239° which did not depress the melting point of an authentic sample. From the residual liquor a 70% yield of Ic was isolated. (2) After dissolving 0.80 g. of 3,5-dimethyl-1-(*N*-phenylcarbamyl)pyrazole[22] in 6.8 ml. of aniline, the solution was similarly treated as in (1) above and afforded identical results. (3) Analogously treated Ib was quantitatively recovered.

Substitution reactions of Ib. Because the techniques employed in the halogenation and nitration reactions of Ib are more or less standard, the synthetic procedures have been condensed in Table I. The following are some additional comments.

(a) When 1.0 g. of Ig was refluxed for 1 hr. in 3.0 ml. of 85% hydrazine hydrate solution, it afforded on cooling and subsequent work-up a mixture of 0.42 g. (91% yield) of diphenylamine, m.p. 54–55°, reported[14] m.p. 54°, mixture m.p. with an authentic sample 54–55°, and 0.40 g. (85% yield) of 4-bromo-3,5-dimethylpyrazole (If), m.p. 117–118°, reported[23] m.p. 118°, which also did not depress the m.p. of an authentic sample, on mixture m.p. determination.

(b) When Ih was analogously hydrazinolyzed, it resulted in a quantitative yield of diphenylamine, a 23% yield of Ic and only traces of Ij, identified by mixture m.p. with an authentic sample.[23] (c) When a sample of the dinitro product (Ik) was refluxed in 3.0 ml. of 85% aqueous hydrazine hydrate solution for 1 hour, the resulting brown reaction liquor, on work-up, gave a 65% yield of Ic and an 80% yield of 4,4′-dinitrodiphenylamine (IIIb), m.p 212–214°, reported[24] m.p. 214°, identified by mixture m.p. with an authentic sample.

Anal. Calcd. for $C_{12}H_9N_3O_4$: C, 55.6; H, 3.5; N, 16.2. Found: C, 55.3; H, 3.8; N, 16.2.

Thus the dinitration product of Ib was identified as 3,5-dimethyl-1-(*N*,*N*-4′4″-dinitrodiphenylcarbamyl)pyrazole (Ik).

CHEMISTRY DEPARTMENT
UNIVERSITY COLLEGE
CORK, IRELAND

CHEMISTRY DEPARTMENT
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIF.

---

[19] T. W. Evans and W. M. Dehn, *J. Am. Chem. Soc.*, 52, 3646 (1930).

[20] Prepared as described by Scott, *et al.*, ref. 9.

[21] Reported by Crosby and Niemann, *loc. cit.*

[22] Synthesized by the method of R. A. Henry and W. Dehn, *J. Am. Chem. Soc.*, 71, 2297 (1949).

[23] Prepared by the method of G. T. Morgan and I. Ackermann, *J. Chem. Soc.*, 1308 (1923).

[24] H. Ryan and P. Ryan, *Proc. Roy. Irish. Acad.*, **34B**, 212 (1919).

4,4′,6,6′-Tetramethyl,-2,2′-bipyridine

ROBERT H. LINNELL[1]

Received February 11, 1957

Recent work[2] on the reaction of sodium with pyridine bases has shown that the 2-position is much more reactive than has heretofore been realized. It should therefore be possible to prepare the new compound 4,4′,6,6′-tetramethyl,-2,2′-bipyridine by

---

[1] Present address: Blawenburg, N. J.

[2] U. S. Patent **2,773,066**, Dec. 4, 1956. To be published.

the reaction of sodium and 2,4-dimethyl pyridine. This new compound should be a Cu(I) specific[3] and would be of interest in studies on the effect of methyl group substitution on complex ions.[4]

EXPERIMENTAL

Two hundred forty ml. of freshly distilled 2,4-dimethyl pyridine was treated with 1.5 g. freshly cut slices of Na metal under reflux at 140°. Gas bubbles appeared at the surface of the Na and a brown color started at this surface and spread throughout the solution turning red-brown, blood red, and finally to a deep blue. After 4 hr. at 140° reaction was assumed complete and air was bubbled into the mixture until the color was a dirty brown, at which time oxidation was believed to be complete. Excess 2,4-dimethyl pyridine was then distilled at atmospheric pressure and the residue vacuum-distilled with the major fraction at 150°, 4–5 mm. pressure. The major fraction was recrystallized from 30–60° ligroin, decolorized with carbon in hot acetone, and finally recrystallized from hexane, yielding 5 g. white needles, m.p. 144–45°.

Anal.[5] Calcd. for $C_{14}H_{16}N_2$: C, 79.20; H, 7.60; N, 13.20. Found: C, 79.43; H, 7.78; N, 13.12.

A monopicrate was formed by adding picric acid in 95% EtOH to the tetramethyl bipyridine in the same solvent. The product was recrystallized from 95% EtOH yielding fine yellow needles with no sharp melting point (dec. starting at 200° and melting about 220°).

Anal.[5] Calcd. for $C_{20}H_{19}N_5O_7$: C, 54.40; H, 4.34; N, 15.96. Found: C, 53.70; H, 4.45; N, 16.27.

Infrared spectra (Nujol mull)[6] of 2,2′-bipyridine and of the assumed 4,4′,6,6′-tetramethyl,-2,2′-bipyridine of this work showed the presence of methyl groups in the latter.

The assumed tetramethyl bipyridine was oxidized with $KMnO_4$, the MnO_2 was removed, the *p*H adjusted with dilute HCl, and the white crystals were purified by recrystallization from H_2O. Repeated recrystallizations did not yield material with a sharp melting point but melting with decomposition near 230°. Trimesitic acid (2,4,6-pyridine-tricarboxylic acid) has a reported m.p. (dec.) of 227°.[7] Berberonic acid (2,4,5-pyridine tricarboxylic acid) has a m.p. of 235° and could arise if the 2,4-dimethyl pyridine had coupled in the 3-position. However coupling in the 3-position is excluded on the basis of complex ion formation.

The assumed 4,4′,6,6′-tetramethyl,-2,2′-bipyridine would not form a complex with Fe (II) ion, as was expected.[8] A complex with Cu(I) ion was formed, having λ_{max} 450 mμ and a molecular extinction coefficient of 6800.[8] This proves the presence of sterically hindered 2,2′-bipyridine linkage.

The tetramethyl bipyridine (0.0755 g.) was dissolved in 25 ml. of HOAc and titrated with 0.06496*N* $HClO_4$ in HOAc with a glass electrode-calomel electrode (MeOH modified) system.[9] Two breaks were found in the titration curve, at 5.64 and 11.25 ml. of titrant. Crystal violet did not give a good visual end point. The theor. mol. wt. of $C_{14}H_{16}N_2$ is 212.3. The titration yields 206.6 and 206.3. It is interesting to note that a similar titration with unsubstituted 2,2′-bipyridine yields only one break in the titration curve, corresponding to the monobasic compound and precipitation takes place. Steric factors probably prevent precipitation of the tetramethyl compound.

Acknowledgment. Thanks are due the Research Corp. for supporting this work. Thanks are also due to Dr. Antoine Zahlan and Mr. Alexander Kaczmarczyk for their help and interest.

TITANIUM ZIRCONIUM CO., INC.
FLEMINGTON, N. J.

---

[3] J. Hoste, *Anal. Chim. Acta*, **4**, 23 (1950).

[4] F. W. Cagle, Jr., and G. F. Smith, *J. Am. Chem. Soc.* **69**, 1860 (1947).

[5] Analyses by Clark Microchemical Laboratory, Urbana, Ill.

[6] The author thanks Mr. John Whalen and the Reynolds Research Laboratory, Winston-Salem, N. C. for the infrared spectra.

[7] Beilstein XXII 185 (5).

[8] Thanks are due Dr. G. Frederick Smith of the University of Illinois for determining these values.

[9] The author thanks Mr. Robert H. Cundiff and the Reynolds Research Laboratory, Winston-Salem, N. C. for these titrations.

The Liebermann Reaction

T. A. TURNEY

Received February 25, 1957

In a study of the reactions of nitrous acid with organic compounds we have recently investigated the Liebermann reaction for phenols. Since our conclusions include some observations not found in the literature we record these here.

The procedure used was that of Mann and Saunders[1] "To one minute crystal of sodium nitrite in a clean dry test tube add 0.5 g. of phenol and heat very gently for about 20 seconds; allow to cool and add twice the volume of concentrated sulphuric acid. On rotating the tube slowly in order to mix the contents, a deep green or blue coloration develops (sometimes only after a few minutes). Dilute cautiously with water; the solution turns red. Now add excess of sodium hydroxide solution, the green or blue color reappears."

This note gives some rationalization of the procedure as well as the inferences that can be drawn from the test.

The active reagent is the nitrosyl ion formed from sodium nitrite and concentrated sulfuric acid. In the preliminary heating the nitrite is covered by the phenol preventing its loss as nitrous fumes. With the more acidic phenols there is sometimes some reaction at this stage which does not affect the test. The heating is unnecessary for liquid phenols. The reaction is carried out under heterogeneous conditions to prevent the sulfonation of the phenol. The product is an indophenol formed by condensation of initially formed nitrosophenol and phenol. This condensation does not occur readily with less than 85% (w/w) sulfuric acid. A transient red color due to the intermediate is often observed before the formation of the blue or green color.

If a *phenol* gives a positive Liebermann reaction (*i.e.* blue or green in concentrated sulfuric acid, red in dilute sulfuric acid, blue or green in alkalies) then

---

[1] F. G. Mann and B. C. Saunders, *Practical Organic Chemistry* 2nd Edition, Longmans Green and Co., London, 1938, p. 218.