tallization from common organic solvents impractical. Distillation of these compounds had to be performed below 1 mm. to prevent decomposition.

As a result of this study, five new secondary or tertiary amines and related derivatives have been prepared and characterized for the first time. The findings also indicate that other *N*-substituted alkyl-aryl ether derivatives of *N*-benzyl-2-aminomethyl-1,4-benzodioxane can be prepared by the method developed in the preparation of the original members of this series.

EXPERIMENTAL

N-Benzyl-2-aminomethyl-1,4-benzodioxane. A 36.8 g. (0.2 mole) portion of 2-chloromethyl-1,4-benzodioxane was added dropwise with stirring, under reflux, during 2.5 hr. to 85.6 g. (0.8 mole) of benzylamine; the mixture was refluxed an additional 1.5 hr., and then cooled to room temperature. Upon the addition of 200 g. of 6*N* hydrochloric acid, a precipitate of secondary amine hydrochloride was obtained. This precipitate was collected and washed with water and ether to remove the excess benzylamine hydrochloride and other impurities. The crude product was then recrystallized from hot water. The free secondary amine was obtained as a viscous oil by neutralization of the hydrochloride salt with sodium bicarbonate. The oil was extracted with ether and the ether then removed by evaporation. The residue was distilled at 180–200° in a Hickmann molecular still at 1 mm. pressure. The yield was 36 g. (70.5%) of a clear viscous liquid with d_4^{25} of 1.1448 and n_D^{25} of 1.5778. Upon prolonged cooling the compound solidified to a white crystalline product, melting at 41°.

Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 75.3; H, 6.67; N, 5.59; M.R., 74.7; mol. wt. 255. Found: C, 75.6; H, 6.98; N, 5.49; M.R. 75.6; mol. wt. 253.

The hydrochloride salt melted at 185° and the hydrobromide salt melted at 214°.

The benzoyl and the benzenesulfonyl derivatives of *N*-benzyl-2-aminomethyl-1,4-benzodioxane, were prepared for further characterization of the above compound. A 5.1 g. (0.02 mole) portion of *N*-benzyl-2-aminomethyl-1,4-benzodioxane was stirred for 0.5 hr. with 5.2 g. (0.04 mole) of benzoyl chloride at 100°, 30 ml. of 10% aqueous sodium hydroxide was then added and the heating continued for an additional 1.5 hr. Upon cooling, the sodium hydroxide solution was decanted, and the remaining precipitate was washed three times with 30 ml. portions of 10% aqueous sodium hydroxide. The remaining product was dissolved in 30 ml. of ether, the solution washed first with 6*N* hydrochloric acid and then with water, and finally dried over anhydrous sodium sulfate. The resulting solution was filtered, the ether evaporated, and the residue distilled at 0.05 mm. in a Hickmann molecular still, at 250–60°, yielding a slightly yellow, extremely viscous oil that solidified below −5°, and had n_D^{25} of 1.5895.

Anal. Calcd. for $C_{23}H_{21}O_3N$: C, 76.88; H, 5.85; N, 3.90; mol. wt. 359. Found: C, 76.53; H, 5.56; N, 4.19; mol. wt. 353.

The benzenesulfonyl derivative was similarly prepared by stirring 5.1 g. (0.02 mole) of *N*-benzyl-2-aminomethyl-1,4-benzodioxane at 100° for 0.5 hr. with 7.1 g. (0.04 mole) of benzenesulfonyl chloride. Thirty ml. of 10% aqueous sodium hydroxide was then added and the heating continued for an additional 1.5 hr. Upon cooling, the sodium hydroxide solution was decanted, and the residue washed three times with 30 ml. portions of 10% aqueous sodium hydroxide. The remaining product was dissolved in 30 ml. of ether, the solution washed first with 6*N* hydrochloric acid, then with water, and finally the ether evaporated. The residue changed from a yellow oil to a white crystalline product when warmed with ethanol. The crystals were triturated several times with ethanol and water and dried, yielding a final derivative melting at 84°.

Anal. Calcd. for $C_{22}H_{21}O_4N$: C, 66.84; H, 5.32; N, 3.54; mol. wt. 395. Found: C, 66.86; H, 5.24; N, 3.73; mol. wt. 399.

N-(2-Phenoxyethyl)-N-benzyl-2-aminomethyl-1,4-benzodioxane. A 10.8 g. (0.04 mole) portion of *N*-benzyl-2-aminomethyl-1,4-benzodioxane and 6 g. (0.03 mole) of phenoxyethyl bromide was heated with stirring at 120° for 6 hr. The reaction mixture was then cooled and triturated with ether and the ether mixture filtered to remove the hydrobromide salt of *N*-benzyl-2-aminomethyl-1,4-benzodioxane. Upon the addition of 20 ml. of 6*N* hydrochloric acid, the hydrochloride salt of *N*-(2-phenoxyethyl)-*N*-benzyl-2-aminomethyl-1,4-benzodioxane separated from the ether as a slightly yellow, very viscous oil. After the salt had been washed with water and ether, it was heated in water and treated with sodium bicarbonate to release the free amine. The free amine was extracted from the mixture with ether, the ether solution washed with water, dried over anhydrous sodium sulfate and filtered. The ether was distilled off, and the residue distilled at 220–240°, in a Hickmann molecular still at 0.05 mm., yielding a pale yellow viscous liquid with n_D^{27} of 1.5820, and d_4^{27} of 1.1415 and which solidified to a white crystalline solid on prolonged standing and melted at 43°.

Anal. Calcd. for $C_{24}H_{25}O_3N$: C, 76.80; H, 6.67; N, 3.73; M.R. 108.9; mol. wt. 375. Found: C, 76.97; H, 6.87; N, 3.38; M.R. 108.76; mol. wt. 372.

N-(2-o-Toloxyethyl)-N-benzyl-2-aminomethyl-1,4-benzodioxane. This compound was prepared and purified by a procedure similar to that described immediately above for N-(2-phenoxyethyl)-N-benzyl-2-aminomethyl-1,4-benzodioxane, except *o*-toloxyethyl bromide was used in place of phenoxyethyl bromide. The product was a pale yellow viscous oil, with a n_D^{27} of 1.5790, and d_4^{27} of 1.1342.

Anal. Calcd. for $C_{25}H_{27}O_3N$: C, 77.12; H, 6.94; N, 3.60; M.R., 113.5; mol. wt. 389. Found: C, 77.47; H, 6.55; N, 3.32; M.R., 112.7; mol. wt. 384.

SCHOOL OF CHEMICAL TECHNOLOGY
NORTH DAKOTA STATE COLLEGE
FARGO, N. D.

Studies in the Pyrazole Series. IX.[1] Aminolytic and Substitution Reactions of 3,5-Dimethyl-1-(*N*,*N*-diphenylcarbamyl)-pyrazole

F. L. SCOTT,[2] A. AHEARNE, AND J. REILLY

Received January 28, 1957

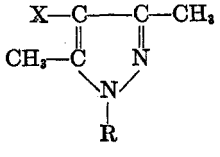
While the solvolytic deacylation reactions of 1-guanyl- and related pyrazoles[1] have been ascribed to a so-called $B_{AC}2$ type[3] mechanism, no unequivocal evidence has been obtained to exclude from

(1) Part VIII: F. L. Scott, *J. Org. Chem.*, 22, 1568 (1957).

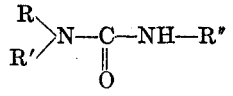
(2) To whom inquiries concerning reprints are to be sent. Present address, Pennsalt Chem. Corp., Whitemarsh Research Labs., Box 4388, Phila. 18, Pa.

(3) See C. K. Ingold, *Structure and Mechanisms in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 752 *et seq.*, wherein the $B_{AC}2$ mechanism is defined as a base-induced bimolecular hydrolysis of esters with acyl scission.

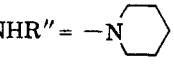
consideration mechanisms involving anionic intermediates such as Ia. The present work was an effort to demonstrate that at least such deacylations need not *necessarily* involve the formation of anionic intermediates, and that the $B_{AC}2$ type mechanism can be sufficiently effective therein. Accordingly, the prototype (Ib) of a new class of pyrazoles, *viz.*, the 1-(*N*,*N*-diphenylcarbamyl) type, wherein the formation of such intermediates as Ia is structurally prohibited, was synthesized and its solvolysis reactions were examined. It proved extremely resistant to ethanolysis,[4] to base-induced hydrolysis by either acetate or hydroxide ions, and to aminolysis by a variety of bases in ethanolic solution. However, use of certain bases as both solvents and reactants did effect decarbamylation of Ib. Thus, when Ib was refluxed for 1 hr. in a 20-molar proportion of either *n*-amylamine or *n*-butylamine, without further solvent, it afforded the corresponding 1,1-diphenyl-3-alkylureas (IIa and b) in 85 and 75% yields, respectively, as well as 3,5-dimethylpyrazole (Ic) in 80% yields. These successful aminolyses clearly demonstrate that the solvolytic deacylation of 1-acylpyrazoles can occur without the necessary intervention of an anionic intermediate.[5] Even under these forcing conditions, Ib remained relatively unreactive, however. Thus it was



Ia*, R = $C(=NH)-\overset{\ominus}{N}-R'$
Ib*, R = $C(=O)-N(C_6H_5)_2$
Ic*, R = H
Id*, R = $C(=O)-NHR'$, where R′ = NH_2 or $CH_2C_6H_5$
Ie, X = Cl, R = $C(=O)-N(C_6H_5)_2$
If, X = Br, R = H
Ig, X = Br, R = $C(=O)-N(C_6H_5)_2$
Ih, X = I, R = $C(=O)-N(C_6H_5)_2$
Ij, X = I, R = H
Ik*, R = $C(=O)-N(C_6H_4NO_2-p)_2$
Il, X = Br, R as in Ik
Im*, R = $C(=O)-N(C_6H_4NH_2-p)_2$
Those symbols starred (*) have X = H

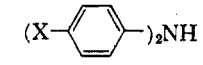


IIa*, R″ = *n*-C_5H_{11}
IIb*, R″ = *n*-C_4H_9



IIc*, NHR″ = −N⟨ ⟩

IId*, R″ = NH_2
IIe, R = R″ = $CH_2C_6H_5$, R′ = H
IIf*, R″ = $CH_2C_6H_5$
Those symbols starred (*) have R = R′ = C_6H_5



IIIa, X = H
IIIb, X = NO_2

unaffected after one hour's refluxing in such bases as aniline, cyclohexylamine, morpholine, or phenylhydrazine. In piperidine as solvent, Ib gave a 30% yield of Ic while only a trace quantity of the expected piperidyl derivative (IIc) was isolated. While this lack of aminolytic reactivity of Ib may be due to its inability to receive base-catalysis, its stability could also be due to steric effects, the three bulky rings inhibiting the $B_{AC}2$ reaction of the central carbonyl group.[6]

Two anomalous reactions were encountered in the aminolyses of Ib. Thus, when refluxed in hydrazine, hydrate solution Ib did not yield the expected 4,4-diphenylsemicarbazide (IId) but gave instead a 95% yield of diphenylamine (IIIa), as well as 80% Ic. However, we found that under identical conditions IId itself is quantitatively hydrazinolyzed to diphenylamine. Secondly when refluxed in benzylamine Ib afforded 1,3-dibenzylurea (IIe) in 70% yield. However, under similar conditions, the anticipated product 1,1-diphenyl-3-benzylurea (IIf) also readily aminolyzes to IIe.[7] Hence both of these reactions are still not inconsistent with the operation of a preliminary $B_{AC}2$ reaction of Ib. Whether this involved the expulsion of pyrazolide ion with the production of a substituted urea, or the expulsion of diphenylamide ion to yield initially a 1-(*N*-substituted carbamyl)pyrazole such as Id, followed by its further aminolysis,[8,9] has not been established.

(4) After maintaining a solution of Ib in ethanol for 28 days at 75.0°C., its spectral characteristics were preserved within the following limits, λ_{max} 236 (±0.9) mμ, ϵ_{max} 16,830 (±340). The absorption spectrum of diphenylurethane is λ_{max} 238 mμ, ϵ_{max} 13,500. For further details of the kinetics of solvolysis (*sic*) of Ib and related substances, see F. L. Scott, *Chimia* (*Switz.*) **11**, 163 (1957) and F. L. Scott and R. Rubin, forthcoming paper in this series.

(5) This lability is most probably due to the anionic stability of pyrazolide ion. In related acyclic systems, this, or a comparable, labilizing moiety is absent and hence the necessity for base-catalysis therein. See D. G. Crosby and C. Niemann, *J. Am. Chem. Soc.*, **76**, 4458 (1954) for further discussions of such acyclic cases.

(6) See *e.g.*, F. H. Wetzel, J. G. Miller, and A. R. Day, *J. Am. Chem. Soc.*, **75**, 1150 (1953) and H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(7) This observation was made in a study of the aminolytic reactions of *N*,*N*-diphenylcarbamyl azide; see F. L. Scott and M. T. Scott, *J. Am. Chem. Soc.*, in press.

(8) We are indebted to a referee for a reminder of this fact.

(9) See F. L. Scott, D. G. O'Donovan, M. R. Kennedy, and J. Reilly, *J. Org. Chem.*, **22**, 820 (1957). The point under consideration is whether pyrazolide ion or another anion, *e.g.*, diphenylamide ion in the present instance, may compete for expulsion from the intermediary adduct of a $B_{AC}2$ process. A major determining factor ought to be the anionic stabilities of the competing moieties, which are of course reflected in the strengths of the corresponding conjugate acids. From available data in the literature the pK_a values for pyrazole and diphenylamine may be estimated as being 11–13 and 23, respectively. This would attribute to

We have commented elsewhere[9] on the general possibility of this latter reaction.

Some substitution reactions of Ib were also examined. Its reaction in chloroform with an excess of chlorine gave some of the corresponding 4-chloro-derivative (Ie) together with some resinous material whose structure was not further pursued. With bromine and iodine reaction was smoother and gave the corresponding monohalogenated derivatives in quantitative yields. The bromination product hydrazinolyzed, in an excess of hydrazine hydrate, to yield 4-bromo-3,5-dimethylpyrazole (If) and diphenylamine (IIIa) and was accordingly identified as 4-bromo-3,5-dimethyl-1-(*N*,*N*-diphenylcarbamyl)pyrazole (Ig). The iodination product was analogously regarded as Ih though its identification was rendered somewhat anomalous by the fact that its hydrazinolysis resulted in diphenylamine and largely 3,5-dimethylpyrazole,[10] only traces of 4-iodo-3,5-dimethylpyrazole (Ij) being detected. When Ib was nitrated under strongly acidic conditions, it afforded a dinitroderivative in 80% yield. This product hydrazinolyzed to Ic and 4,4′-dinitrodiphenylamine (IIIb) and was thereby itself recognized as 3,5-dimethyl-1-(*N*,*N*-4,′4″-dinitrodiphenylcarbamyl)pyrazole (Ik). When Ik was brominated and Ig was nitrated they were converted into a common product (Il), a result which further confirms the orientations offered. This difference in the behavior of Ib toward halogenation and nitration with exclusive heterocyclic reaction in the former process[11] and solely phenyl substitution in the latter[12] is attributable primarily to the deactivation by protonation of the substituted pyrazole nucleus under the strongly acidic nitration conditions. This deactivation is not realized to any appreciable extent under the mild acidities of the halogenation techniques adopted.

EXPERIMENTAL[13]

3,5-Dimethyl-1-(N,N-diphenylcarbamyl)pyrazole (Ib). To 2.0 g. of 4,4-diphenylsemicarbazide dissolved in 25 ml. of ethanol was added 0.8 ml. (1 molar equivalent) of freshly distilled acetylacetone. On allowing this solution to stand overnight at room temperature 1.65 g. of Ib separated. This after 2 recrystallizations from 95% ethanol melted at 134–135°.

Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.2; H, 5.8; N, 14.4. Found: C, 73.9; H, 5.7; N, 14.8.

A further quantity, 0.54 g. (total yield 85%), of Ib was obtained on work-up of the mother liquor. No change either in product or in yield was obtained when the reacting substances were refluxed together in ethanolic solution for 3 hours prior to the isolation of the product.

Aminolyses of Ib. (*1*) *In ethanolic or aqueous solution.* When Ib was refluxed with 1 molar equivalent of aniline, *n*-butylamine, *n*-hexylamine, hydrazine hydrate or phenylhydrazine for 30–60 min. in ethanolic solution, it was recovered in 90–100% yields. When it was refluxed for 2 hr. with an excess of 4*N* sodium acetate solution, or of 1*N* hydrochloric acid or of 2.5*N* sodium hydroxide solution it was quantitatively recovered.

(*2*) *In amines as solvents.* When Ib was dissolved in a 20-molar proportion of either aniline or phenylhydrazine, without additional solvent, the reaction liquor being maintained at 60° for 1 hr., Ib was recovered in 100 and 80% yields, respectively. With hydrazine hydrate as nucleophile under these conditions, 80% Ib was again recovered but also a 10% yield of 3,5-dimethylpyrazole (Ic) was obtained. The following example illustrates the final forcing technique adopted. To 2.0 g. of Ib was added 8 ml. of 85% aqueous hydrazine hydrate solution—this was a twenty-fold molar proportion of nucleophile—and the whole was then refluxed for 1 hr. This solution after being allowed to cool overnight on work-up yielded 1.10 g. (95% yield) of diphenylamine (IIIa), m.p. 54–55°, reported[14] m.p. 54°, whose mixture m.p. with an authentic sample was not depressed, and an 80% yield of 3,5-dimethylpyrazole (Ic), m.p. 105–106°, reported[15] m.p. 107°, similarly identified.[16] The expected main product in this reaction was not IIIa but 4,4-diphenylsemicarbazide (IId). The stability of the latter under the above conditions was then checked. It was hydrazinolyzed under the above treatment to IIIa in 98% yield. The other expected fragment, *i.e.*, carbohydrazide, was not isolated.

Under the above conditions, *n*-amylamine resulted in a 70% yield of Ic as well as an 85% yield of 1,1-diphenyl-3-*n*-amylurea (IIa), m.p. 70–71°, reported[17] m.p. 70–71°.

Anal. Calcd. for $C_{18}H_{22}N_2O$: C, 76.6; H, 7.8; N, 9.9. Found: C, 76.3; H, 7.5; N, 9.4.

When analogously treated, *n*-butylamine formed IIb and Ic in 75 and 60% yields, respectively. After recrystallization from aqueous ethanol, IIb melted at 93–94°.

Anal. Calcd. for $C_{17}H_{20}N_2O$: C, 76.1; H, 7.5; N, 10.4. Found: C, 75.6; H, 7.5; N, 9.9.

Finally, when Ib was similarly treated with benzylamine, except that a 90-min. reflux period was used, it resulted in a 75% yield of Ic and a 70% yield of 1,3-dibenzylurea (IIe), m.p. 164–166°, reported[18] m.p. 165–167°.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 75.0; H, 6.7. Found: C, 75.0; H, 6.5.

Some related reactions. (a) When Ib was refluxed for 1-hr. periods without further solvent other than a 20-molar proportion of the following bases, aniline, cyclohexylamine, morpholine, phenylhydrazine, or piperidine it was recovered in 100, 100, 75, and 68% yields, respectively. Only with the last amine were some deacylation products detected, *viz.*, a

pyrazolide ion, an anionic stability greater by at least a factor of 10^{10} over diphenylamide ion and may help to explain the deacylation pattern of Ib.

(10) Compare L. F. Audrieth and B. A. Ogg, *The Chemistry of Hydrazine*, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 134–9.

(11) Compare the halogenation of 1- and 3-phenylpyrazoles, A. Michaelis and G. Käding, *Ann.*, **373**, 202 (1900) and previous papers, and K. v. Auwers and B. Ottens, *Ber.*, **58**, 2072 (1925).

(12) Compare K. v. Auwers and H. Mauss, *Ann.*, **452**, 182 (1927); E. Harrison, *J. Soc. Chem. Ind.*, **54**, 282T (1935); I. M. Kogan and D. F. Kutepov, *Zhur. Obshchei Khim.*, **21**, 1297 (1951).

(13) All melting points are uncorrected. All microanalyses are by Drs. Wieler and Strauss, Oxford, England.

(14) I. Heilbron and H. M. Bunbury, *Dictionary of Organic Compounds*, 4th ed., Eyre and Spottiswoode, London, 1953, p. 402.

(15) R. H. Wiley and P. E. Hexner, *Org. Syntheses*, **31**, 43 (1951).

(16) In all the aminolysis experiments wherein 3,5-dimethylpyrazole was obtained, it was identified both by mixture melting point with an authentic sample, and by mixture of its picrate with an authentic sample.

(17) Scott and Scott, *loc. cit.*

(18) P. P. Grad and R. J. Dunn, *Anal. Chem.*, **25**, 1211 (1953).

TABLE I

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

Reaction	Product	Molecular Formula	M.P., °C.	Yield, %	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen 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.