TABLE I

MALONDIAMIDES

Malondiamides	M.p., °C.	Formula	Analyses, % Calcd. C	H	N	Found C	H	N
p-Chlorobenzyl	244	$C_{10}H_{11}O_2N_2Cl$	..	...	12.4	..	...	12.5
p-Bromobenzyl	245	$C_{10}H_{11}O_2N_2Br$	..	...	10.3	..	...	9.9
p-Methoxybenzyl	216-217	$C_{11}H_{14}O_3N_2$	..	...	12.6	..	...	12.9
3,4-Dichlorobenzyl	212	$C_{10}H_{10}O_2N_2Cl_2$	46.0	3.8	10.7	46.4	3.9	10.2
Phenyl	226-228	$C_9H_{10}O_2N_2$	60.7	5.6	15.7	60.7	5.8	16.0

TABLE II

MALONONITRILES (III)

R	Yield, %	M.p. or b.p., °C.	Formula	Analyses, % Calcd. N	Found N
CH_2CH_3	80	b. 100 (20 mm.)[a]	$C_5H_6N_2$	..	..
$(CH_2)_3CH_3$	70	b. 120 (20 mm.)	$C_7H_{10}N_2$	23.0	23.0
$CH_2C_6H_5$	47	m. 79[b]	$C_{10}H_8N_2$	..	..
$CH_2C_6H_4Cl$-*p*	55	89	$C_{10}H_7N_2Cl$	14.7	14.4
$CH_2C_6H_4Br$-*p*	50	90-91	$C_{10}H_7N_2Br$	11.9	11.6
$CH_2C_6H_3Cl_2$-3,4	60	[c]	$C_{10}H_6N_2Cl_2$	..	..
$CH_2C_6H_4(OCH_3)$-*p*	48	70-72	$C_{11}H_{10}ON_2$	15.1	14.7
C_6H_5	47	67[d]	$C_9H_6N_2$	..	..

[a] J. C. Hessler, *Am. Chem. J.*, **22**, 185 (1899), gives b.p. 90–91° (20 mm.). [b] J. C. Hessler[a] gives m.p. 91°; E. Hantzsch and G. Osswald, *Ber.*, **32**, 649 (1899), give 78–79°. [c] Viscous oil, did not crystallize. [d] J. C. Hessler, *Am. Chem. J.*, **32**, 123 (1904), gives 68–69°.

TABLE III

2,4,6-TRIAMINO-5-SUBSTITUTED PYRIMIDINES (I)

R	Yield, %	M.p., °C.	Formula	Analyses, % Calcd. C	H	N	Found C	H	N
C_2H_5	92	190[a]	$C_6H_{11}N_5$	..	...	..	..	...	..
C_4H_9-*n*	90	199	$C_8H_{15}N_5$	53.0	8.3	..	53.4	8.3	..
$CH_2C_6H_5$	85	191–192	$C_{11}H_{13}N_5$	61.4	6.0	32.6	61.6	6.0	32.6
$CH_2C_6H_4Cl$-*p*	98	218	$C_{11}H_{12}N_5Cl$	..	...	28.1	..	...	28.4
$CH_2C_6H_4Br$-*p*	85	235	$C_{11}H_{12}N_5Br$	..	...	23.8	..	...	24.1
$CH_2C_6H_4(OCH_3)$-*p*	80	218-219	$C_{12}H_{15}ON_5$	..	...	28.6	..	...	28.5
$CH_2C_6H_3Cl_2$-3,4	92	255	$C_{11}H_{11}N_5Cl_2$	46.5	3.9	24.6	46.5	3.9	24.6

[a] Merck (ref. 9) and v. Merkatz (ref. 5) give m.p. 190°.

triamino-5-*p*-chlorobenzylpyrimidine (I, R = $CH_2C_6H_4Cl(p)$), however, gave consistent results of a ± grade on repeated trials.

Experimental

Malonic Esters.—The malonic esters, where not commercially available, were prepared by the action of the halide on sodium malonic ester in ethanol. They were distilled to separate any disubstituted ester and then converted to the amides directly as shown below. It should be noted that any of the disubstituted ester present would not be converted to the amide under the conditions used.[10] Ethyl *p*-methoxybenzylmalonate was prepared by reduction of ethyl *p*-methoxybenzalmalonate.[14]

Malondiamides.—The malondiamides were prepared by the previously described method.[10] They are listed in Table I.

Malononitriles.—The malononitriles were prepared by the distillation of the corresponding diamides with phosphorus pentoxide. The preparation of benzyl malononitrile is given as an example. The properties of these compounds are given in Table II.

Benzylmalononitrile.—Benzylmalondiamide[10] (30 g.) was mixed well with phosphorus pentoxide (60 g.) and the mixture distilled at 250° (bath temp.) (20 mm.). The distillate solidified on cooling. It was redistilled to give a colorless oil (17 g.) b.p. 220–225° (23 mm.) which solidified to colorless crystals, m.p. 79°.

2,4,6-Triaminopyrimidines (I).—These compounds were prepared by refluxing the malononitriles (III) with guanidine in alcohol. The preparation of 2,4,6-triamino-5-benzylpyrimidine (I, R = $CH_2C_6H_5$) is given as an example. The compounds are listed in Table III.

To a solution of sodium ethoxide prepared by dissolving sodium (3.4 g.) in ethanol (100 ml.) was added guanidine hydrochloride (9.5 g.) and benzylmalononitrile (14 g.) and the mixture was refluxed for three hours. After filtration the solution was allowed to cool when the pyrimidine (15 g.) crystallized as plates. Recrystallization from ethanol gave colorless plates, m.p. 191–192°.

Reaction of Phenylmalononitrile (III, R = C_6H_5) with Guanidine.—The nitrile (6 g.) was added to a solution of guanidine (from the hydrochloride (4.0 g.)) in ethanol (75 ml.) and the solution refluxed for 5 hours. On cooling and standing crystals separated which after recrystallization from ethanol–ether melted at 139–140° (Found: N, 41.6%).

Acknowledgment.—Thanks are due S. W. Blackman, N. Martinez, Jr., and Pauline Kulka for the analyses recorded in this paper.

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(14) E. Knoevenagel and A. Grous, *Ber.*, **31**, 2594 (1898).

The Halogenation of 3,5-Dimethyl-1-(2′-quinolyl)-pyrazole

BY F. L. SCOTT, K. M. CROWLEY AND J. REILLY

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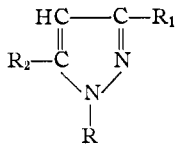
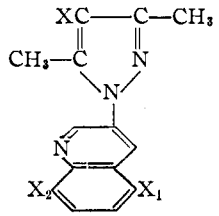
The behavior of the 1-substituted pyrazoles varies from the very stable aryl (or alkyl) types to the relatively unstable carbamyl class.

We have recently shown that both the 1-nitroguanyl[1] (I, R = —C(=NH)—NHNO$_2$) and the 1-guanylpyrazoles[2,3] (I, R = —C(=NH)—NH$_2$) resemble the 1-carbamyl type—being readily susceptible to fission. The 1-heterocyclic pyrazoles have been synthesized for the extension of this comparison. The 1-tetrazolyl compound (I, R = –CHN$_4$) has been described elsewhere.[4] The present communication deals with the prototype of the 1-(2′-quinolyl) class (I, R = C$_9$H$_6$N(2′)).



I



II

With this type of compound, however, at least three isomeric products may be obtained in reaction with cationoid reagents, *e.g.*, in halogenation, substitution may occur at the 4-, 5′- or 8′-position. No kinetic data are available for the accurate orientation of the monohalogenated compounds obtained.

The heterocyclic portion of the 1-quinoline substituent may be considered[5] as a deactivated nucleus toward such reagents; therefore, the competing centers in these halogenations are those of a benzene ring and a pyrazole ring. These centers[6] compete in the halogenation of 3,5-dimethyl-1-phenylpyrazole (I, R$_1$,R$_2$ = CH$_3$, R = C$_6$H$_5$) and 1-phenylpyrazole (I, R$_1$,R$_2$ = H, R = C$_6$H$_5$), and Balbiano[7] reports merely the formation of the 4-halopyrazole in these instances. With the latter compound trihalogenation may be effected to yield 1-phenyl-3,4,5-tribromopyrazole without substituting in the phenyl nucleus.

On the basis of present evidence then the products described below may be allotted the structure (II, X = Cl/Br/I, X$_I$, X$_2$ = H). Experiments are at present being undertaken to determine by degradation the unequivocal structure of these materials and, secondly, the proportion of the respective isomers (if any) formed. Irrespective of the final orientation, the experiments described below show that the 1-(2′-quinolyl) substituent approximates to the 1-aryl type in the stability of its attachment to the pyrazole ring.

(1) F. L. Scott, M. T. Kennedy and J. Reilly, *Nature*, **169**, 72 (1952).

(2) F. L. Scott and J. Reilly, Pyrazoles I, THIS JOURNAL, **74**, in press (1952).

(3) F. L. Scott, C. M. B. Murphy and J. Reilly, *Nature*, **167**, 1037 (1951).

(4) F. L. Scott, D. G. O'Donovan and J. Reilly, *J. App. Chem.*, in press.

(5) Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, 1949, p. 185. See also Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 371.

(6) A closer analogy would have been the halogenation of 3,5-dimethyl-1(2′-(1′-nitro)-naphthyl)-pyrazole or allied substances, Such data are not available.

(7) Balbiano, *Ber.*, **23**, 1452 (1890); Balviano, *Gazz. chim. ital.*, **19**, 128, 133 (1889); see also Severini, *Atti Accad. Lincei* **5**, 1, II, 393 (1892).

Experimental[8]

3,5-Dimethyl-1-(2′-quinolyl)-pyrazole (A).—4.35 g. (0.03 mole) of 2-quinolylhydrazine was dissolved in 120 ml. of 95% ethanol and to the solution was added 3.06 ml. (0.03 mole) of acetylacetone. This mixture was refluxed for 3 hours and the dark colored solution obtained, was then evaporated to half-bulk, on a steam-bath. On cooling at 0°, crude A (4.7 g., m.p. 51–56°) separated; the filtrate was diluted with water and a further 1.02 g. of A was obtained. After recrystallization from petroleum ether (b.p. 40–60°) using a little animal charcoal, it was obtained as white needles of m.p. 57°.

Anal. Calcd. for C$_{14}$H$_{13}$N$_3$: C, 75.3; H, 5.8; N, 18.8. Found: C, 75.3; H, 6.2; N, 18.5.

It was characterized as its **picrate**, which after recrystallization from aqueous ethanol, was obtained as an orange micro-crystalline powder of m.p. 159°.

Anal. Calcd. for C$_{20}$H$_{16}$N$_6$O$_7$: C, 53.1; H, 3.5; N, 18.5. Found: C, 53.3; H, 3.6; N, 18.7.

Chlorination of A.—Through a solution of 0.5 g. (0.002 mole) of A, in 5 ml. of dry chloroform was bubbled an excess of dry chlorine. On evaporating the chloroform, after reaction had ceased, 0.48 g. of a yellow crystalline material of m.p. 46–49° was obtained. This was a mixture of the chloro derivative and unreacted A, and after fractional recrystallization from petroleum ether, it was obtained as a white amorphous solid of m.p. 72.5°.

Anal. Calcd. for C$_{14}$H$_{12}$ClN: C, 65.2; H, 4.7; Cl, 13.8; N, 16.3. Found: C, 64.8; H, 4.6; Cl, 14.1; N, 16.5.

Bromination of A.—To 0.5 g. (0.002 mole) of A, dissolved in 10 ml. of carbon tetrachloride was added 0.115 ml. (0.002 mole) of bromine, with stirring. Some yellow oil separated and on evaporating off the carbon tetrachloride in a stream of air, 0.81 g. of a substance, of m.p. 189–191° was obtained. This bromo-compound (which contained excess bromine) was recrystallized from glacial acetic acid as small feathery needles, of m.p. 108°.

Anal. Calcd. for C$_{14}$H$_{12}$BrN$_3$: C, 55.6; H, 3.9; Br, 26.5; N, 13.9. Found: C, 55.6; H, 3.8; Br, 26.6; N, 13.5.

Iodination of A.—To 0.5 g. (0.002 mole) of A, in 50 ml. of glacial acetic acid were added 0.23 g. (0.0014 mole) of potassium iodine and 0.48 g. (0.007 mole) of potassium iodate and an additional 5 ml. of acetic acid. The mixture was refluxed until the very dark color developed initially had lightened to a pale orange-yellow—this took 11 minutes. The inorganic, undissolved solid was then filtered off, and the solution allowed to stand for 24 hours at room temperature. 0.54 g. of material of m.p. 125° separated and a further 0.14 g. was precipitated from the filtrate on the addition of water. *Anal.* Calcd. for C$_{14}$H$_{12}$N$_3$I: C, 48.1; H, 3.4; N, 12.1; I, 36.4. Found: C, 48.9; H, 3.5; N, 12.7. I, 35.4.

(8) Analyses are by Drs. Weiler and Strauss, Oxford, England. All melting points are uncorrected.

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Synthesis of Lignin Model Compounds

BY BISWANATH SEN

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The work of Kratzl and co-workers[1,2] on the sulfonation of chalcones and other α,β-unsaturated ketones shows that these compounds are readily sulfonated. However, it is not yet known whether pyran or furan ring formation of the three-carbon side chain would change the reactivity of the α,β-unsaturated ketonic grouping toward bisulfite. With this end in view, the present work describes

(1) K. Kratzl and H. Daubner, *Ber.*, **77**, 519 (1944).

(2) K. Kratzl, H. Daubner and U. Siegens, *Monatsh.*, **77**, 146 (1947).