in 80 ml. of water, and the solution was adjusted to *p*H 7 with dilute ammonium hydroxide. The mixture was allowed to stand, and the precipitate was filtered, washed with water, and dried at 60° to yield 5.2 g. of colorless 6-chloropurine. The ultraviolet absorption spectra[21] were characteristic of that of 6-chloropurine.

Anal. Calcd. for $C_5H_3N_4Cl$: N, 36.2. Found: N, 36.4.

Preparation of 8-Hydroxy-6-methylsulfonylpurine from 6,8-Bis-methylthiopurine.—Three grams of 6,8-bis-methylthiopurine[6] was placed in 100 ml. of a 27:75% methanol–water solution. The solution was stirred, and chlorine gas was passed into it for approximately 1 hr. The reaction temperature was maintained <15°. The precipitate was finally filtered, and the wet crude product then was placed in approximately 60 ml. of boiling water and heated for 10 min. The solution was cooled, and the precipitate was filtered, washed with water, and dried at 110° to yield 1.5 g. of product, m.p. > 300°.

Anal. Calcd. for $C_6H_6N_4O_3S$: C, 33.7; H, 2.8; N, 26.2. Found: C, 34.2; H, 2.6; N, 26.4.

TEMPE, ARIZ.

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[21] A. Bendich, P. J. Russell, Jr., and J. J. Fox, THIS JOURNAL, **76**, 6073 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

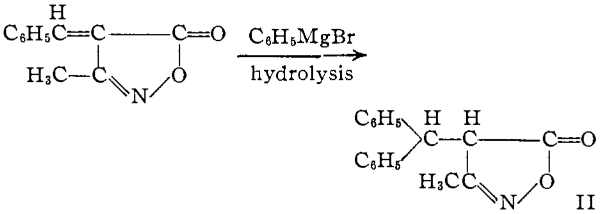
Action of Grignard Reagents. XIV.[1] Action of Organomagnesium Compounds on 1-Phenyl-3-methyl-4-arylidene-5-pyrazolones. Their Behavior toward Aromatic Secondary Amines and Aromatic Thiols

BY AHMED MUSTAFA, WAFIA ASKER, AHMED FATHY A. SHALABY, SAMIR A. KHATTAB AND ZEIN E. SELIM

RECEIVED MARCH 23, 1959

Grignard reagents add to the double bond of the lateral chain of the highly colored 1-phenyl-3-methyl-4-arylidene-5-pyrazolones (III) to give, after hydrolysis, colorless products, believed to have structure IV. Similarly, addition reaction was observed when III are allowed to react with piperidine, with morpholine or with aromatic thiols to give V and VI, respectively.

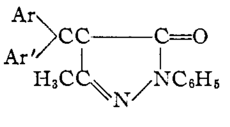
Panizzi[2] has shown that the isoxazolone ring in 3-methyl-4-benzylideneisoxazolone (I) is stable toward the action of phenylmagnesium bromide and only the double bond of the lateral chain of I enters into reaction, yielding 3-methyl-4-diphenylmethyl-5-isoxazolone (II).



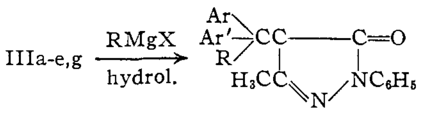
II

In extension of the work by one of us on the action of Grignard reagents on heterocyclic nitrogen compounds,[3,4] the action of these reagents on 1-phenyl-3-methyl-4-arylidene-5-pyrazolones (IIIa-e) and on 1-phenyl-3-methyl-4-diphenylmethylene-5-pyrazolone (IIIg), the nitrogen analogs of I, now has been investigated. Thus, when the orange IIIa is treated with phenylmagnesium bromide, followed by hydrolysis, a colorless product believed to be 1-phenyl-3-methyl-4-diphenylmethyl-5-pyrazolone (IVa) is obtained.

The structure of IVa, which is taken as an example of compounds IVa-o, is inferred from the fact that it is colorless. Also, the finding that IVc is obtained by the action of phenylmagnesium bromide on IIIc and by the action of *p*-tolylmagnesium iodide on IIIa may be taken in favor of the assigned structure for the Grignard products (*cf.* IV).



IIIa, Ar = C_6H_5; Ar' = H
b, Ar = $C_6H_4OCH_3$-*p*; Ar' = H
c, Ar = $C_6H_4CH_3$-*p*; Ar' = H
d, Ar = C_6H_4Cl-*o*; Ar' = H
e, Ar = $C_6H_3{:}O_2CH_2$; Ar' = H
f, Ar = $C_6H_4NO_2$-*p*; Ar' = H
g, Ar = Ar' = C_6H_5



IVa, Ar = C_6H_5; Ar' = H; R = C_6H_5
b, Ar = C_6H_5; Ar' = H; R = $C_6H_4OCH_3$-*p*
c, Ar = C_6H_5; Ar' = H; R = $C_6H_4CH_3$-*p*
d, Ar = C_6H_5; Ar' = H; R = CH_3
e, Ar = $C_6H_4OCH_3$-*p*; Ar' = H; R = $C_6H_4OCH_3$-*p*
f, Ar = $C_6H_4OCH_3$-*p*; Ar' = H; R = $C_6H_4CH_3$-*p*
g, Ar = $C_6H_4CH_3$-*p*; Ar' = H; R = $C_6H_4CH_3$-*p*
h, Ar = C_6H_4Cl-*o*; Ar' = H; R = C_6H_5
i, Ar = C_6H_4Cl-*o*; Ar' = H; R = $C_6H_4OCH_3$-*p*
j, Ar = C_6H_4Cl-*o*; Ar' = H; R = $C_6H_4CH_3$-*p*
k, Ar = $C_6H_3{:}\ O_2CH_2$; Ar' = H; R = C_6H_5
l, Ar = $C_6H_3{:}O_2CH_2$; Ar' = H; R = CH_3
m, Ar = Ar' = R = C_6H_5
n, Ar = Ar' = C_6H_5; R = $C_6H_4OCH_3$-*p*
o, Ar = Ar' = C_6H_5; R = CH_3

1-Phenyl-3-methyl-5-pyrazolone[5] proved to be stable toward the action of phenylmagnesium bromide under similar experimental conditions, thus showing the stability of the hetero-ring toward the action of Grignard reagents; IVa was identical with the product obtained by the catalytic reduction of IIIg. The activity of the vinyl group in III may be compared with the activity of the olefinic double bond in I, and the stability of the 5-membered heterocyclic ring in I and III is in contrast to the ready opening of the oxazolone ring in 2-phenyl-4-arylidene-2-oxazoline-5-ones.[4]

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[1] For part XIII *cf.* W. Asker, A. Mustafa, M. K. Hilmy and M. A. Allam, *J. Org. Chem.*, **23**, 2002 (1958).

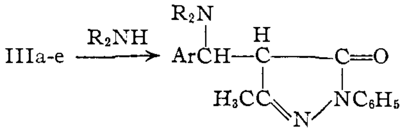
[2] L. Panizzi, *Gazz. chim. ital.*, **76**, 44 (1946).

[3] A. Mustafa, W. Asker, M. Kamel, A. F. A. Shalaby and A. E. Hassan, THIS JOURNAL, **77**, 1612 (1955); A. Mustafa, W. Asker and O. H. His, *ibid.*, **77**, 5127 (1955); A. Mustafa, A. F. A. Shalaby and M. E. Sobhy, *J. Org. Chem.*, **23**, 2929 (1958).

[4] A. Mustafa and A. H. E. Harhash, *ibid.*, **21**, 575 (1956).

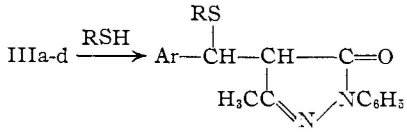
[5] *Cf.* its probable tautomeric structures on the basis of ultraviolet absorption spectra (D. Biquard and M. P. Grammaticakis, *Bull. soc. chim. France*, **8**, 246 (1941)); Valyashke and Bliznyukev, *J. Gen. Chem.*, (*U.S.S.R.*), *11*, 559 (1941); Westoo, *Acta Chem. Scand.*, **6**, 1499 (1952); R. C. Elderfield "Heterocyclic Compounds," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 122.

Addition of secondary amines, *e.g.*, piperidine, morpholine, etc., to α,β-unsaturated compounds is well known.[6,7] It was our first objective to learn whether the compounds IIIa-e are also capable of undergoing conjugate additions of secondary amines. We have found that when the colored benzene solution of IIIa is treated with piperidine, at room temperature, the color almost disappears; addition of light petroleum effects the separation of a colorless crystalline substance, believed to have structure Va. Similarly IIIb-e undergo addition reactions with piperidine and morpholine under the same experimental conditions and it was also possible to obtain adducts Va-j. In no case have we been able to record the formation of isomeric racemates which should exist in such adducts.[8] The adducts V are colorless products, decompose near the melting points yielding the corresponding colored 1-phenyl-3-methyl-4-arylidene-5-pyrazolone.

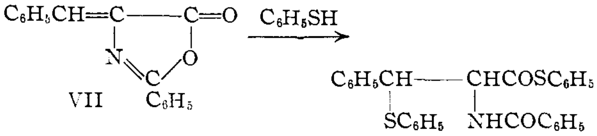


Va, Ar = C_6H_5; R_2 = $C_5H_{10}N$ (piperidyl)
b, Ar = C_6H_5; R_2 = C_4H_8ON (morphenyl)
c, Ar = $C_6H_4OCH_3$-*p*; R_2 = $C_5H_{10}N$
d, Ar = $C_6H_3OCH_3$-*p*; R_2 = C_4H_8ON
e, Ar = $C_6H_4CH_3$-*p*; R_2 = $C_5H_{10}N$
f, Ar = $C_6H_4CH_3$-*p*; R_2 = C_4H_8ON
g, Ar = C_6H_4Cl-*o*; R_2 = $C_5H_{10}N$
h, Ar = C_6H_4Cl-*o*; R_2 = C_4H_8ON
i, Ar = $C_6H_3{:}O_2CH_2$; R_2 = $C_5H_{10}N$
j, Ar = $C_6H_4NO_2$-*p*; R_2 = $C_5H_{10}N$

Ruhmann[9] has reported that thiophenol reacts with IIIa in the presence or even in the absence of piperidine to give the adduct VIa. In contrast to the marked stability of the hetero-ring in VI toward the action of aromatic thiols, the hetero-ring in 2-phenyl-4-benzal-5-oxazolone (VII) is readily opened by thiophenol to give VIII.[10] The addition of thiophenol to the lateral double bond in VII is parallel to the addition of the same reagent to the double bond in III. We were able to obtain the product described by Ruhmann when a benzene solution of IIIa is allowed to react with thiophenol in absence of piperidine; but in presence of piperidine Va was obtained in an almost quantitative yield. Similarly, IIIa-d and IIIf reacted with aromatic thiols in absence of catalyst to give the corresponding addition products (VIb-o). The thiol adducts VI are stable under normal conditions, but are decomposed into the original components by refluxing with alcoholic potassium hydroxide (*cf.* the elimination of the mercaptan molecule from thiol adducts, for, *e.g.*, the elimination of *p*-thiocresol from its adducts with benzalacetophenone by the action of alcoholic sodium hydroxide solution[11] and also by heating above their melting points).



VIa, Ar = C_6H_5; R = C_6H_5
b, Ar = C_6H_5; R = $C_6H_4CH_3$-*o*
c, Ar = C_6H_5; R = $C_6H_4CH_3$-*p*
d, Ar = $C_6H_4OCH_3$-*p*; R = C_6H_5
e, Ar = $C_6H_4OCH_3$-*p*; R = $C_6H_4CH_3$-*o*
f, Ar = $C_6H_4OCH_3$-*p*; R = $C_6H_4CH_3$-*p*
g, Ar = $C_6H_4CH_3$-*p*; R = C_6H_5
h, Ar = $C_6H_4CH_3$-*p*; R = $C_6H_4CH_3$-*o*
i, Ar = $C_6H_4CH_3$-*p*; R = $C_6H_4CH_3$-*p*
j, Ar = C_6H_4Cl-*o*; R = C_6H_5
k, Ar = C_6H_4Cl-*o*; R = $C_6H_4CH_3$-*o*
l, Ar = C_6H_4Cl-*o*; R = $C_6H_4CH_3$-*p*
m, Ar = $C_6H_4NO_2$-*p*; R = C_6H_5
n, Ar = $C_6H_4NO_2$-*p*; R = $C_6H_4CH_3$-*o*
o, Ar = $C_6H_4NO_2$-*p*; R = $C_6H_4CH_3$-*p*



VII

VIII

Experimental

Action of Grignard Reagents on 1-Phenyl-3-methyl-4-arylidene-5-pyrazolone (III).—The following illustrates the general procedure; to an ethereal solution of phenylmagnesium bromide (prepared from 0.9 g. of magnesium, 8 g. of bromobenzene and 40 ml. of dry ether) was added a suspension of 1 g. of IIIa[12] in 30 ml. of dry ether. The red color of IIIa readily disappeared. The reaction mixture was refluxed (steam-bath) for one hour, set aside at room temperature overnight, then it was poured slowly into a cold saturated aqueous ammonium chloride solution and extracted with ether. The ethereal layer was dried over anhydrous sodium sulfate. The ether extract on concentration deposited colorless crystals; a further crop was obtained on complete evaporation. The whole product was recrystallised from a mixture of benzene and petroleum ether (b.p. 50–70°) to give colorless crystals of IVa, m.p. 220° (*cf.* Table I).

Attempted Action of Phenylmagnesium Bromide on 1-Phenyl-3-methyl-5-pyrazolone.—The Grignard reagent is prepared as described above; then 1 g. of 1-phenyl-3-methyl-5-pyrazolone is added to it. When the reaction mixture was worked up, the starting material was recovered essentially unchanged (m.p. and mixed m.p. determinations).

Catalytic Hydrogenation of IIIg.—A mixture of 1 g. of 5% palladium on barium sulfate[13] in 15 ml. of absolute ethyl alcohol was exposed to nascent hydrogen till it acquired a black coat, then 1 g. of IIIg[14] was dissolved in 20 ml. of absolute ethyl alcohol and added to it. The reaction mixture was exposed to the current of hydrogen under reduced pressure for 2 hours till the red color of the solution disappeared. The alcoholic solution was separated by filtration and on evaporation a colorless residue was left. It was recrystallized from ethyl alcohol into colorless crystals and identified as IVa (m.p. and mixed m.p. determinations).

Action of Secondary Amines on 1-Phenyl-3-methyl-4-arylidene-5-pyrazolones (IIIa-f). General Procedure.—A mixture of 0.005 mole of IIIa and 0.005 mole of the appropriate secondary amine in 30 ml. of dry benzene was allowed to stand at room temperature overnight. The red color

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[6] J. Loevenich and H. Gerber, *Ber.*, **63**, 1707 (1930); J. Loevenich, J. Koch and U. Pucknat, *ibid.*, **63**, 636 (1930); R. L. Heath and J. D. Rose, *J. Chem. Soc.*, 1486 (1947).

[7] *Cf.* the addition of secondary amines to benzalacetophenone; R. Georgi and A. Schwyzer, *J. prakt. Chim.*, **86**, 273 (1912); V. E. Stewart and C. B. Pollard, THIS JOURNAL, **58**, 1980 (1936); **59**, 2702 (1937); N. H. Cromwell and J. S. Burch, *ibid.*, **66**, 872 (1944); N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

[8] Similar conjugate additions usually have yielded only one diastereoisomer. See, however, P. L. Southwick and J. E. Anderson, THIS JOURNAL, **79**, 6222 (1957).

[9] S. Ruhmann, *J. Chem. Soc.*, **87**, 468 (1905).

[10] A. Mustafa, A. H. E. Harhash and M. Kamel, THIS JOURNAL, **77**, 3860 (1955).

[11] B. H. Nicolet, *ibid.*, **53**, 3066 (1931).

[12] L. Knorr, *Ann.*, **238**, 179 (1887).

[13] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 685.

[14] H. Heiduschda and O. Rothbacker, *J. Prakt. Chem.*, **84**, 537 (1911).

TABLE I

ACTION OF GRIGNARD REAGENTS ON 1-PHENYL-3-METHYL-4-ARYLIDENE-5-PYRAZOLONES

Pyrazolone derivative	Grignard reagent	Product	Solvent	M.p.,[a] °C.	Yield, %	Color with H_2SO_4	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIa	C_6H_5	IVa	Benzene–petr. (50–70°)	220	60	Yellow	$C_{23}H_{20}N_2O$	81.17	80.64	5.88	5.94	8.23	8.32		
IIIa	$C_6H_4OCH_3$-*p*	IVb	Alcohol	180	58	Orange-red	$C_{24}H_{22}N_2O_2$	77.83	77.62	5.94	6.00	7.56	7.41		
IIIa	$C_6H_4CH_3$-*p*	IVc	Alcohol	198	70	Yellow	$C_{24}H_{22}N_2O$	81.35	80.87	6.21	6.31	7.90	7.88		
IIIa	CH_3	IVd	Alc. ether	117	62	Yellow	$C_{18}H_{18}N_2O$	77.69	77.20	6.47	6.55	10.07	9.98		
IIIb[b]	C_6H_5	IVb													
IIIb	$C_6H_4OCH_3$-*p*	IVc	Petr. ether (120)	265	52	Orange	$C_{25}H_{24}N_2O_3$	75.00	74.88	6.00	6.01	7.00	6.92		
IIIb	$C_6H_4CH_3$-*p*	IVf	Petr. (90–120)	109	66	Orange	$C_{25}H_{24}N_2O_2$	78.12	78.02	6.25	6.30	7.29	7.09		
IIIc[c]	C_6H_5	IVc													
IIIc	$C_6H_4OCH_3$-*p*	IVf													
IIIc	C_6H_4–CH_3-*p*	IVg	Alcohol	178	85	Yellow	$C_{25}H_{24}N_2O$	81.52	81.60	6.52	6.53	7.60	7.51		
IIId[d]	C_6H_5	IVh	Alcohol	192	88	Yell.-brown	$C_{23}H_{19}N_2OCl$	73.69	73.66	5.07	5.00	7.47	7.21	9.47	9.33
IIId	$C_6H_4OCH_3$-*p*	IVi	Alcohol	180	80	Pale yell.	$C_{24}H_{21}N_2O_2Cl$	71.19	71.00	5.19	5.22	6.92	6.81	8.77	8.81
IIId	$C_6H_4CH_3$-*p*	IVj	Alcohol	190	86	Orange	$C_{24}H_{21}N_2OCl$	74.13	74.20	5.41	5.29	7.20	7.13	9.13	9.00
IIIe[e]	C_6H_5	IVk	Dil. alc.	195	65	Dark red	$C_{24}H_{20}N_2O_3$	75.00	74.98	5.20	5.37	7.29	7.36		
IIIe	CH_3	IVL	Alcohol	163	70	Pink	$C_{19}H_{18}N_2O_3$	70.80	71.30	5.59	5.87	8.69	8.65		
IIIg	C_6H_5	IVm	Benzene	233	60	Yellow	$C_{29}H_{24}N_2O$	83.65	83.15	5.76	5.86	6.73	6.70		
IIIg	$C_6H_4OCH_3$-*p*	IVn	Alcohol	172	55	Yellow	$C_{30}H_{26}N_2O_2$	80.71	10.11	5.82	5.78	6.27	6.59		
IIIg	CH_3	IVo	Alc.–ether	148	65	Yellow	$C_{24}H_{22}N_2O$	81.35	81.10	6.21	6.38	7.90	7.91		

[a] All the melting points are uncorrected. [b] G. W. Sawdey (to Eastman Kodak Co.), U. S. Patent 2,706,683, April 19, 1955; *C. A.*, **49**, 9421 (1955). [c] Prepared after Sawdey,. m.p. 115° (from alc.). *Anal.* Calcd. for $C_{18}H_{16}N_2O$: C, 78.26; H, 5.79; N, 10.14. Found: C, 78.29; H, 5.68; N, 10.13. [d] Prepared after Sawdey, m.p. 146° (from alc.). *Anal.* Calcd. for $C_{17}H_{13}N_2OCl$: C, 68.80; H, 4.38; N, 9.43; Cl, 11.97. Found: C, 69.00; H, 4.36; N, 9.38; Cl, 12.00. [e] J. Tambor, *Ber.*, **33**, 869 (1900).

TABLE II

ACTION OF SECONDARY AMINES TO 1-PHENYL-3-METHYL-4-ARYLIDENE-5-PYRAZOLONES

Pyrazolone derivative	Secondary amine	Product	M.p.,[a] °C.	Yield, %	Color with H_2SO_4	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIa	$C_5H_{11}N$[c]	Va	209	78	Yellow	$C_{22}H_{25}N_3O$	76.08	75.88	7.20	7.13	12.10	12.23
	C_4H_9NO[d]	Vb	163	68	No color	$C_{21}H_{23}N_3O_2$	72.20	72.17	6.59	6.37	12.03	11.89
IIIb	$C_5H_{11}N$	Vc	213	70	Pale yell.	$C_{23}H_{27}N_3O_2$	73.20	73.15	7.16	7.21	11.14	11.00
	C_4H_9NO	Vd	185	60	No color	$C_{22}H_{25}N_3O_3$	69.65	69.40	6.59	6.49	11.08	10.99
IIIc	$C_5H_{11}N$	Ve	204	85	No color	$C_{23}H_{27}N_3O$	76.45	76.40	7.47	7.39	11.63	11.30
	C_4H_9NO	Vf	210	81	No color	$C_{22}H_{25}N_3O_2$	72.72	72.49	6.88	6.69	11.57	11.49
IIId	$C_5H_{11}N$	Vg	199	90	No color	$C_{22}H_{24}N_3OCl$[e]	69.20	69.19	6.29	6.11	11.00	10.79
	C_4H_9NO	Vh	233	87	No color	$C_{21}H_{22}N_3O_2Cl$[f]	65.71	65.54	5.73	5.55	10.95	10.76
IIIe	$C_5H_{11}N$	Vi	218	70	Red-brown	$C_{23}H_{25}N_3O_3$	70.58	70.07	6.39	6.30	10.74	11.05
IIIf[b]	$C_5H_{11}N$	Vj	208	73	No color	$C_{22}H_{24}N_4O_3$	67.34	67.43	6.12	6.15	14.28	14.82

[a] All the melting points are uncorrected. [b] H. Heiduschka and O. Rothacker, *J. prakt. Chem.*, **84,** 537 (1911). [c] Piperidine. [d] Morpholine. [e] Cl, calcd. 9.30, found 9.25. [f] Cl, calcd. 9.25, found 9.07.

TABLE III

ACTION OF AROMATIC THIOLS ON 1-PHENYL-3-METHYL-4-ARYLIDENE-5-PYRAZOLONES

Pyrazolone derivative	Thio R =	Product	Solvent	M.p.,[a] °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
IIIa	$C_6H_4CH_3$-*o*	VIb	Alcohol	137	60	$C_{24}H_{22}N_2OS$	74.61	74.58	5.69	5.60	7.25	7.30	8.29	8.31
IIIa	$C_6H_4CH_3$-*p*	VIc	Alcohol	129	78	$C_{24}H_{22}N_2OS$		74.63		5.59		7.29		8.09
IIIb	C_6H_5	VId	Alcohol	103	60	$C_{24}H_{22}N_2O_2S$	71.64	71.59	5.47	5.44	6.96	6.90	7.96	7.91
IIIb	$C_6H_4CH_3$-*o*	VIe	Alcohol	96	55	$C_{25}H_{24}N_2O_2S$	72.11	72.06	5.76	5.59	6.73	6.79	7.69	7.61
IIIb	$C_6H_4CH_3$-*p*	VIf	Alcohol	131	68	$C_{25}H_{24}N_2O_2S$		72.18		5.40		6.66		7.71
IIIc	C_6H_5	VIg	Alcohol	138	70	$C_{24}H_{22}N_2OS$	74.61	74.50	5.69	5.70	7.25	7.22	8.29	8.08
IIIc	$C_6H_4CH_3$-*o*	VIh	Benzene–petr. ether (50–70°)	136	60	$C_{25}H_{24}N_2OS$	75.00	75.10	6.00	5.89	7.00	6.91	8.00	8.09
IIIc	$C_6H_4CH_3$-*p*	VIi	Alcohol	145	78	$C_{25}H_{24}N_2OS$		75.09		6.03		6.88		7.98
IIId	C_6H_5	VIj	$CHCl_3$ in petr. ether (50–70°)	156	73	$C_{23}H_{19}N_2OSCl$[b]	67.89	67.90	4.67	4.73	6.88	6.69	7.87	7.80
IIId	$C_6H_4CH_3$-*o*	VIk	Alcohol	140	66	$C_{24}H_{21}N_2OSCl$[c]	68.48	68.51	4.99	4.88	6.65	6.71	7.60	7.61
IIId	$C_6H_4CH_3$-*p*	VIl	Alcohol	158	70	$C_{24}H_{21}N_4OSCl$[d]		68.40		4.90		6.48		7.38
IIIf	C_6H_5	VIm	Benzene–petr. ether	125	65	$C_{23}H_{19}N_3O_3S$	66.18	66.00	4.55	4.40	10.07	10.29	7.67	7.49
IIIf	$C_6H_4CH_3$-*o*	VIn	Benzene–petr. (50–70°)	118	65	$C_{24}H_{21}N_3O_3S$	66.82	66.90	4.87	4.77	9.74	9.66	7.42	7.30
IIIf	$C_6H_4CH_3$-*p*	VIo	Benzene–petr. (50–70°)	97	73	$C_{24}H_{21}N_3O_3S$		66.76		4.92		9.70		7.28

[a] All the melting points are uncorrected. [b] Cl, calcd. 8.73, found 8.80. [c] Cl, calcd. 8.44, found 8.38. [d] Cl, found, 8.51.

gradually faded and on addition of 8 ml. of petroleum ether (b.p. 50–70°) to the reaction mixture, colorless crystals separated, which were collected by filtration and recrystallized from ethyl alcohol (*cf.* Table II).

Thermal Decomposition of Va.—The adduct Va (1 g.) was heated at 195–200° (bath-temperature) in a test-tube-shaped vessel for 20 minutes and then allowed to cool. The bottom of the reaction vessel contained a red oily residue which solidified after being washed with petroleum ether (p.b. 50–70°). The solid (*ca.* 0.6 g.) so obtained was crystallized from ethyl alcohol and identified as IIIa (m.p. and mixed m.p. determinations).

Action of Aromatic Thiols on IIIa-d, f. General Procedure.—To a solution of the appropriate 5-pyrazolone derivative (1 g.) in 30 ml. of dry benzene was added 1 g. of the appropriate thiol and the reaction mixture was left at room temperature overnight. The deep red color gradually faded and colorless crystals deposited, which were collected by filtration and recrystallized from ethyl alcohol (*cf.* Table III).

The thiol adducts listed in Table III are colorless, soluble in benzene and insoluble in petroleum ether (b.p. 50–70°). They are insoluble in cold aqueous sodium hydroxide solution (10%). The thiol adducts, on treating with concd. H_2SO_4, give a deep orange color which turns to blood-red slowly.

Action of Potassium Hydroxide on VIc.—The thiol adduct (0.5 g.) was refluxed with 50 ml. of alcoholic potassium hydroxide solution (4%) for 4 hours. The reaction mixture was poured into ice-cold water, acidified with dilute hydrochloric acid and extracted with ether. The ether extract gave, on shaking with lead acetate solution, yellow crystals of the lead salt of *p*-thiocresol (m.p. and mixed m.p. determinations). The ether solution after thorough washing with water and then evaporation, gave a red solid substance (*ca.* 0.2 g.) which was identified as IIIa.

Thermal Decomposition of VIc.—The pyrolysis was carried out as described in case of Va at 110–115° (bath temperature); IIIa was obtained in an almost quantitative yield.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Synthesis of Carbazoles from 3-Vinylindoles with Tetracyanoethylene and Dimethyl Acetylenedicarboxylate

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The tricyanovinylation of indole has been extended to substituted indoles, including 1-methylindole, 2-methylindole and 1,2-dimethylindole, giving the corresponding 3-tricyanovinylindoles (Ib-Id) in good yields. Several derivatives of the latter are described. Tricyanovinylation of skatole occurred in the 1-position, giving 3-methyl-1-tricyanovinylindole (Ie) in 77% yield. 3-Tricyanovinylindole (Ia) and 1-methyl-3-tricyanovinylindole (Ib), acting as dienes, undergo Diels–Alder reactions with dimethyl acetylenedicarboxylate, resulting in the loss of hydrogen cyanide and forming the corresponding dimethyl 3,4-dicyanocarbazole-1,2-dicarboxylates (X). Saponification of the latter, followed by esterification of the resulting tetraacids with diazomethane, yielded the corresponding tetramethyl carbazole-1,2,3,4-tetracarboxylates (XI). The one derived from indole (XIa) was prepared independently, along with three minor products (XVIII–XX), by the reaction of indole with dimethyl acetylenedicarboxylate in 1:2 molar ratio. The latter reaction probably involves an intermediate 3-vinylindole (XII) which acts as a diene in a Diels–Alder reaction with a second molecule of dimethyl acetylenedicarboxylate. These reactions appear to represent the first examples of the 3-vinylindole synthesis of carbazoles. Decarboxylation of the carbazole tetraacids by pyrolysis with soda-lime gave carbazole in both cases, N-demethylation having occurred in the N-methyl case. Since N-methylcarbazole does not demethylate under the same conditions, it is suggested that the N-demethylation occurs by intramolecular nucleophilic displacement (in a 6-membered ring transition state) of the methyl group by the neighboring 1-carboxylate anion.

The reaction of tetracyanoethylene with indole, yielding 3-tricyanovinylindole (Ia), has been described previously.[2] By use of boiling benzene as solvent, containing a small amount of pyridine, the

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(2) G. N. Sausen, V. A. Engelhardt and W. J. Middleton, THIS JOURNAL, **80**, 2815 (1958).