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REACTIONS WITH 1,2,3-TRIONE-2-ARYLHYDRAZONES

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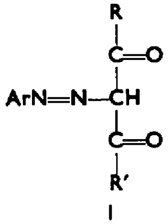
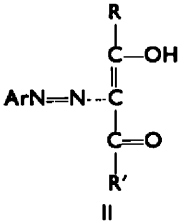
Abstract—Whereas, the pentan-2,3,4-trione-3-arylhydrazones (IVa–d) and 1-phenylbutan-1,2,3-trione-2-arylhydrazones (Va–d) undergo the Mannich reaction with formaldehyde and piperdine, 1,3-diphenylpropan-1,2,3-trione-2-arylhydrazones (VIa–d) are recovered unchanged. The ease of cleavage of the acetyl group during the reaction is stressed. A number of the Mannich-bases (VII) react with aromatic thiols to yield the corresponding sulphur analogues (VIII).

The arylhydrazones of the triones (IV–VI) undergo 1,2-addition of the Grignard reagent, to the acetyl carbonyl group in IV and V and to the benzoyl carbonyl group in VI, to yield Xa-k. Acetophenone is obtained upon chromic acid oxidation of Xa-b; on the other hand, benzophenone is obtained in the case of Xd. Treatment of Xh and Xj with hydrazine hydrate eliminates the tertiary carbinol moiety with the formation of the hydrazones of the corresponding phenylglyoxal arylhydrazones (XIa–b).

β-Diketones couple with aromatic diazonium compounds in alkaline solutions to give "mixed azo compounds",[1] which may have one of the potentially tautomeric structures (I–III); difficult to establish with certainty. However, it is generally assumed that the hydrazone is the stable form whenever coupling occurs at a methyl or a methylene carbon. Recently, Wiley and Jarbo[2] and Tanner[3] have presented IR absorption data which corroborate this view.



I



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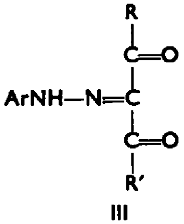

III

A study of the Mannich reaction with a number of 1,2,3-trione-2-arylhydrazones was undertaken. Pentan-2,3,4-trione-3-arylhydrazones (IVa–d), and 1-phenylbutan-1,2,3-trione-2-arylhydrazones (Va–d), all react with formaldehyde to yield products VIIa–h, respectively. On the other hand, (1,3-diphenylpropan-1,2,3-trione-2-arylhydrazones (VIa–d) are recovered in almost quantitative amounts after treatment with the same reagent under the given experimental conditions.

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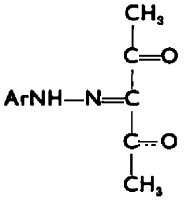
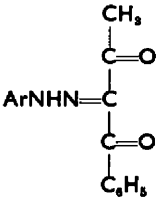
[1] K. Holzach, *Die Aromatischen Diazoverbindungen* p. 141. Enke, Stuttgart (1947); K. H. Saunders, *The Aromatic Diazo-compounds and Their Technical Applications.* (2nd. Edition) p. 209. Edward Arnold (1949).

[2] R. H. Wiley and C. H. Jarbo, Jr., *J. Amer. Chem. Soc.* 77, 403 (1955).

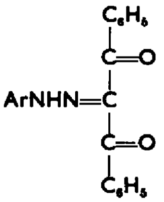
[3] E. M. Tanner, *Spectrochem. Acta* 20 (1959).



IV

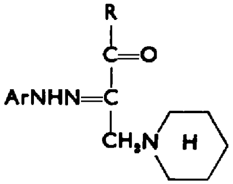


V



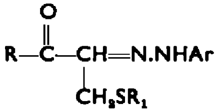
VI

a, Ar = C_6H_5; b, Ar = $C_6H_4CH_3$—o; c, Ar = $C_6H_4CH_3$—m; d, Ar = $C_6H_4CH_3$—p.



VIIa, R = CH_3; Ar = C_6H_5
b, R = CH_3; Ar = $C_6H_4CH_3$-o
c, R = CH_3; Ar = $C_6H_4CH_3$-m
d, R = CH_3; Ar = $C_6H_4CH_3$-p
e, R = Ar = C_6H_5
f, R = C_6H_5; Ar = $C_6H_4CH_3$-o
g, R = C_6H_5; Ar = $C_6H_4CH_3$-m
h, R = C_6H_5; Ar = $C_6H_4CH_3$-p

The Mannich-bases (VIIa–b, d) are ketonic and form the corresponding hydrazones and oximes. Treatment of VIIa,d,g–h with aromatic thiols at 100° results in the formation of the sulphur analogues (VIIIa–g), respectively.[4] The IR spectrum of VIIe, taken as an example of the Mannich-bases, shows absorption at 2·8μ, 3·0μ(m), 6·15μ(s), and 6·25μ(s), and reveals the absence of a carbonyl band below 6·0μ.[5] The Mannich-base, VIIa, now has also been obtained by treatment of pyruvaldehyde-1-phenylhydrazone with formaldehyde.[6]



$$R-\overset{O}{\overset{\|}{C}}-\underset{CH_2SR_1}{C}H=N.NHAr$$

VIIIa, R = CH_3; Ar = C_6H_5; R_1 = $C_6H_4CH_3$-m
b, R = CH_3; Ar = $C_6H_4CH_3$-p; R_1 = $C_6H_4CH_3$-m
c, R = Ar = C_6H_5; R_1 = $C_6H_4CH_3$-m
d, R = R_1 = C_6H_5; Ar = $C_6H_4CH_3$-m
e, R = C_6H_5; Ar = R_1 = $C_6H_4CH_3$-m
f, R = R_1 = C_6H_5; Ar = $C_6H_4CH_3$-p
g, R = C_6H_5; Ar = $C_6H_4CH_3$-p; R_1 = $C_6H_4CH_3$-m

It is of interest to report that α-unsubstituted β-dicarbonyl compounds, e.g., 2,4-pentandione react with formaldehyde to yield an intramolecular aldol condensation product, 4,6-diacetyl-3-hydroxy-3-methylcyclohexanone.[7] Moreover, dibenzoylmethane with secondary amines and formaldehyde, yield not the Mannich-bases,

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[4] Cf. F. Poppelsdorf and S. J. Holt, *J. Chem. Soc.* 1124 (1954); A. Mustafa, W. Asker, A. H. Harhash, K. M. Foda, H. H. Jahine and N. A. Kassab, *Tetrahedron* **20**, 531 (1964).

[5] P. B. Russell, *J. Amer. Chem. Soc.* **75**, 5315 (1953).

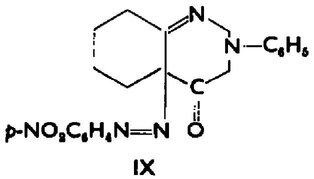
[6] Cf. the formation of methyl formazyl ketone upon treatment of pyruvaldehyde-1-phenylhydrazone with benzenediazonium chloride, E. Bamberger and J. Lorenzen, *Ber. Dtsch. Chem. Ges.* **25**, 3539 (1892).

[7] B. D. Wilson, *J. Org. Chem.* **28**, 315 (1963); J. K. O'Loane, C. M. Combs and R. L. Griffith, *Ibid.* **29**, 1730 (1964).

but 1,1,3,3-tetrabenzoylpropane.[8] Liebermann and Wagner[9] assumed that this reaction proceeds via a Mannich intermediate followed by elimination of the amine in a further condensation.

The ease of cleavage of the acetyl group in the above-reported C-alkylation during the Mannich reaction with IV and V is similar to the cleavage of the acyl group during nitrosation of α-monoalkyl β-keto-esters,[10] the cleavage of the acyl group during treatment of α-substituted β-diketones and β-keto-esters with benzenediazonium chloride (Japp-Klingemann reaction),[11] and the loss of the arylidene group in 4-arylidene-1-aryl-3-methyl-5-pyrazolones by the action of diazonium salts, yielding 4-arylazo derivatives.[12]

Little is known about the cleavage of aromatic acyl groups but they appear more firmly bound than their aliphatic analogues. The elimination of the acetyl group and not the benzoyl group in the Mannich reaction with V resembles the loss of the acetyl group in the Japp-Klingemann reaction with ethyl benzoylacetoacetate and with ethyl phenacetylacetoacetate; thus showing that in such cleavages the acyl group corresponding to the weaker acid is more readily liberated.[11,13] The failure of VIa–d to undergo the Mannich reaction is analogous to IX which does not undergo the Japp-Klingemann transformation, but instead loses the azo function in a reversal of the coupling reaction,[11] and to the instability of ethyl α-methyl-α-N-dimethylaminomethylacetoacetate.[14]



IX

α-Monoalkyl derivatives of acetoacetic and benzoylacetic esters condense with various secondary amines and formaldehyde, at low temperatures, to produce products of the general formula $RCO(R')(CH_2NR_2'')COOC_2H_5$ without the elimination of the acyl group.[14] It seems possible that the elimination of the acetyl group in the Mannich reaction with IV and V, whereby the azo group is attached to a tertiary carbon atom, is necessary to make the hydrazone formation possible. This resembles very closely the coupling of α-methylacetylacetone in the Japp-Klingemann reaction to yield the phenylhydrazone of the diacetyl.[15]

Similar to the base-catalysed cleavage of the acyl group in the Japp-Klingemann

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[8] R. D. Desai, *J. Ind. Chem. Soc.* **10**, 663 (1933); E. C. Hornig and M. G. Hornig, *J. Org. Chem.* **11**, 95 (1946).

[9] S. V. Liebermann and E. C. Wagner, *J. Org. Chem.* **14**, 1001 (1949).

[10] O. Touster, in Adams, *Organic Reactions*, Vol. VII, Chap. 6. J. Wiley, New York (1953).

[11] R. R. Phillips, in Adams, *Organic Reactions*, Vol. X, Chap. 2. J. Wiley, New York (1959).

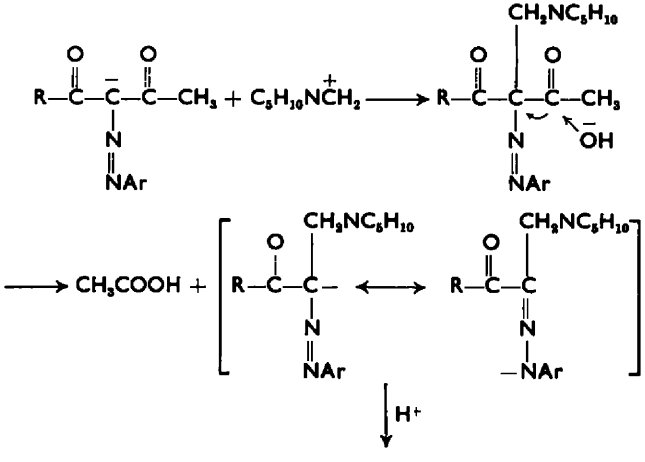
[12] F. Stolz, *Ber. Dtsch. Chem. Ges.* **28**, 623 (1895); G. W. Sawdey, M. K. Ruoff and P. W. Vittum, *J. Amer. Chem. Soc.* **72**, 4947 (1950).

[13] C. Bülow and E. Hailer, *Ber. Dtsch. Chem. Ges.* **35**, 915 (1902).

[14] B. Reichert, *Die Mannich-Reaktion* p. 45. Springer-Verlag, Göttingen (1959); K. Bodendorf, K. J. Krüger and F. Zermal, *Liebig's Ann.* **562**, 1 (1949).

[15] G. Favrel, *Bull. soc. chim. Fr.* [3] **27**, 336 (1902); *C. R. Acad. Sci., Paris ed.* **132**, 41 (1901).

reaction,[11] the Mannich reaction with IV and V may be represented as follows:



VII

The first step undoubtedly occurs as in the Mannich reaction and, although the mechanism of the latter remains in some doubt, it is best represented[9,16] as a direct union of the anion of the active methinyl compound and the cation $C_6H_{10}N\overset{+}{C}H_2$, formed from the condensation product of piperidine and formaldehyde. The elimination of the acetyl group does *not* precede the introduction of the N-piperidinomethyl group, since IVa is recovered almost quantitatively upon refluxing with piperidine or with formaldehyde in the presence or absence of tri-n-propylamine.

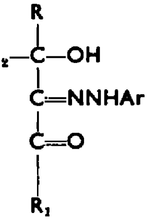
In addition, a study of the reaction of the arylhydrazones of the triones (IV–VI) with arylmagnesium halides was undertaken in order to gain an insight into the structure of the original mixed azo compounds. When IVb is treated with excess phenylmagnesium bromide, 1,2-addition of one mole of the Grignard reagent to the carbonyl group takes place with the formation of Xa. Similarly, Va–b react with one mole of the same reagent to yield Xb–c, respectively. Treatment of VIa–d with phenylmagnesium bromide, or *p*-tolylmagnesium iodide yields Xd–k.[17] The products are pale yellow in colour, do not give a colour with alcoholic ferric chloride or alcoholic copper acetate solution.[18] The IR spectrum of Xd, taken as an example, shows absorption at 2·8μ, 3·0μ(m), 6·15μ(s) and 6·25μ(S), and reveals the absence of a carbonyl band below 6μ.[5]

The Grignard reagent reacts with the carbonyl group of the acetyl moiety in Va–b, and not with the benzoyl moiety, since acetophenone results from the treatment of Xb–c with chromic acid in glacial acetic acid. Benzophenone is formed upon similar treatment of Xd with the same reagent; on the other hand acetophenone is isolated in the case of Xa.

[16] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 581. G. Bell (1953); K. Bodendorf and G. Koralewski, *Arch. Pharm.* **271**, 101 (1933); E. R. Alexander and E. J. Underhill, *J. Amer. Chem. Soc.* **71**, 4014 (1949).

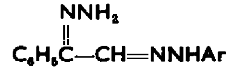
[17] Cf. the 1,2-addition of one mole of phenylmagnesium bromide to dibenzoylmethane, M. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances* p. 386. Prentice-Hall, New York (1954).

[18] L. J. Bellamy and R. F. Branch, *J. Chem. Soc.* 4491 (1954).



Xa, $R = R_1 = CH_3$; $R_2 = C_6H_5$; $Ar = C_6H_4CH_3$-o
b, $R = CH_3$; $R_1 = R_2 = Ar = C_6H_5$
c, $R = CH_3$; $R_1 = R_2 = C_6H_5$; $Ar = C_6H_4CH_3$-o
d, $R = R_1 = R_2 = Ar = C_6H_5$
e, $R = R_1 = Ar = C_6H_5$; $R_2 = C_6H_4CH_3$-p
f, $R = R_1 = R_2 = C_6H_5$; $Ar = C_6H_4CH_3$-o
g, $R = R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$-p; $Ar = C_6H_4CH_3$-o
h, $R = R_1 = R_2 = C_6H_5$; $Ar = C_6H_4CH_3$-m
i, $R = R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$-p; $Ar = C_6H_4CH_3$-m
j, $R = R_1 = R_2 = C_6H_5$; $Ar = C_6H_4CH_3$-p
k, $R = R_1 = C_6H_5$; $R_2 = Ar = C_6H_4CH_3$-p

Treatment of Xh and Xj with hydrazine hydrate gives the hydrazone of the corresponding phenylglyoxal arylhydrazone (XIa–b) with the elimination of the tertiary carbinol moiety. This elimination is similar to the treatment of Xk with hydrazine hydrate and the formation of XIb (see above).

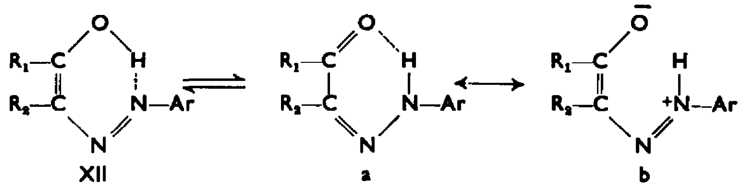


$$C_6H_5\overset{\overset{\displaystyle NNH_2}{\|}}{C}—CH{=}NNHAr$$

XIa, $Ar = C_6H_4CH_3$-m
b, $Ar = C_6H_4CH_3$-p

In the arylhydrazones of the triones (IV–VI) only one carbonyl group is bound in the resonating system XIIIa–b. The other carbonyl group, R_2 in XIII, is free and it is this group that undergoes 1,2-addition with the Grignard reagent.[19] When one of the carbonyl groups in 1,2,3-trione-2-arylhydrazones is a benzoyl group, the other being an acetyl group (cf. V), it would appear that the benzoyl group is held in the resonating system, and is not attacked by the Grignard reagent. Thus, V may be written as XIII ($R_1 = C_6H_5$, $R_2 = COCH_3$). The phenyl group may conjugate with the resonating system thereby lowering the energy of this form. Zwitterionic structures similar to XIIIb were considered by Kuhn[20] to account for the properties of *o*-hydroxyazo compounds. A structure like XII is unlikely since with diazomethane in methanolic ether, 1,2,3-trione-2-arylhydrazones fails to form the corresponding enol ethers.[5]

The work in progress will be the subject of a further communication.



XII a b
XIII

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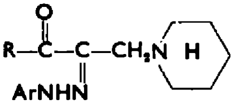
[19] Cf. the formation of epoxides upon treatment of 1,2,3-trione-2-phenylhydrazones with diazomethane, ref. 5.

[20] R. Kuhn, Naturwiss. 20, 632 (1932).

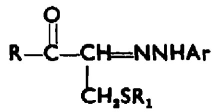
TABLE 1. MANNICH-BASES (VII)



	R	Ar	M.p.[a]	Yield, %	Formula	Carbon, % Found	Carbon, % Calc.	Hydrogen, % Found	Hydrogen, % Calc.	Nitrogen, % Found	Nitrogen, % Calc.
VIIa	CH_3	C_6H_5	104°	65	$C_{15}H_{21}ON_3$	69·59	69·50	8·41	8·11	16·96	16·22
VIIb	CH_3	$C_6H_4CH_3$—o	135°	71	$C_{16}H_{23}ON_3$	70·13	70·33	8·11	8·42	15·30	15·38
VIIc	CH_3	$C_6H_4CH_3$—m	67°	62	$C_{16}H_{23}ON_3$	70·24	70·33	8·21	8·42	15·29	15·38
VIId	CH_3	$C_6H_4CH_3$—p	125°	69	$C_{16}H_{23}ON_3$	70·76	70·33	8·67	8·42	15·08	15·38
VIIe	C_6H_5	C_6H_5	85°	64	$C_{20}H_{23}ON_3$	74·63	74·77	7·07	7·17	12·97	13·08
VIIf	C_6H_5	$C_6H_4CH_3$—o	101°	67	$C_{21}H_{25}ON_3$	75·00	75·22	7·12	7·46	12·14	12·54
VIIg	C_6H_5	$C_6H_4CH_3$—m	102°	65	$C_{21}H_{25}ON_3$	74·89	75·22	7·31	7·46	12·38	12·54
VIIh	C_6H_5	$C_6H_4CH_3$—p	116°	66	$C_{21}H_{25}ON_3$	74·66	75·22	7·44	7·46	12·83	12·54

[a] All m.ps are uncorrected.

TABLE 2. ARYLTHIOMETHYL DERIVATIVES (VIII)



$R-C(=O)-CH(CH_2SR_1)=NNHAr$

	R	R$_1$	Ar	M.p.[a]	Yield %	Formula	Carbon, % Found	Carbon, % Calc.	Hydrogen, % Found	Hydrogen, % Calc.	Nitrogen, % Found	Nitrogen, % Calc.	Sulphur, % Found	Sulphur, % Calc.
VIIIa	CH_3	$C_6H_4CH_3$—m	C_6H_5	81°	53	$C_{17}H_{19}ON_2S$	68·26	68·23	6·11	6·35	9·60	9·36	10·68	10·70
VIIIb	CH_3	$C_6H_4CH_3$—m	$C_6H_4CH_3$—p	97°	55	$C_{18}H_{21}ON_2S$	68·89	69·01	6·56	6·71	8·71	8·94	10·10	10·22
VIIIc	C_6H_5	$C_6H_4CH_3$—m	C_6H_5	130°	61	$C_{22}H_{21}ON_2S$	73·01	73·13	5·63	5·82	7·54	7·76	8·64	8·86
VIIId	C_6H_5	C_6H_5	$C_6H_4CH_3$—m	126°	58	$C_{22}H_{21}ON_2S$	72·88	73·13	5·51	5·82	7·66	7·76	8·64	8·86
VIIIe	C_6H_5	$C_6H_4CH_3$—m	$C_6H_4CH_3$—m	128°	63	$C_{23}H_{22}ON_2S$	73·55	73·60	6·01	6·13	7·46	7·47	8·56	8·54
VIIIf	C_6H_5	C_6H_5	$C_6H_4CH_3$—p	125°	57	$C_{22}H_{21}ON_2S$	73·43	73·13	5·57	5·82	7·94	7·76	8·53	8·86
VIIIg	C_6H_5	$C_6H_4CH_3$—m	$C_6H_4CH_3$—p	104°	52	$C_{23}H_{23}ON_2S$	73·89	73·60	5·99	6·13	7·57	7·47	8·56	8·54

[a] All m.ps are uncorrected.

TABLE 3. GRIGNARD PRODUCTS (X) FROM 1,2,3-TRIONE-2-ARYLHYDRAZONES (IV–VI)

Arylhydrazone	Grignard reagent, R=	Product	Solvent[a] of Cryst.	M.p.[b]	Yield %	Formula	Carbon, % Found	Carbon, % Calc.	Hydrogen, % Found	Hydrogen, % Calc.	Nitrogen, % Found	Nitrogen, % Calc.
IVb	phenyl	Xa	B	135°	56	$C_{18}H_{20}O_2N_2$	73·17	72·97	6·44	6·76	9·33	9·46
Va	phenyl	Xb	D	185°	57	$C_{22}H_{20}O_2N_2$	77·17	76·74	6·35	5·81	7·79	8·14
Vb	phenyl	Xc	B	140°	54	$C_{23}H_{22}O_2N_2$	76·59	77·09	6·01	6·15	7·72	7·82
VIa	phenyl	Xd	C	166°	61	$C_{27}H_{22}O_2N_2$	79·54	79·80	5·21	5·42	6·81	6·90
VIa	*p*-tolyl	Xe	C	177°	58	$C_{28}H_{24}O_2N_2$	79·86	80·00	5·34	5·72	6·56	6·67
VIb	phenyl	Xf	A	187°	64	$C_{28}H_{24}O_2N_2$	79·74	80·00	5·61	5·72	6·60	6·67
VIb	*p*-tolyl	Xg	A	184°	61	$C_{29}H_{26}O_2N_2$	79·85	80·18	5·74	5·99	6·16	6·45
VIc	phenyl	Xh	C	173°	54	$C_{28}H_{24}O_2N_2$	79·96	80·00	5·90	5·72	6·84	6·67
VIc	*p*-tolyl	Xi	C	189°	56	$C_{29}H_{26}O_2N_2$	80·23	80·18	5·90	5·99	6·56	6·45
VId	phenyl	Xj	A	174°	59	$C_{28}H_{24}O_2N_2$	79·64	80·00	5·49	5·72	6·43	6·67
VId	*p*-tolyl	Xk	C	163°	58	$C_{29}H_{26}O_2N_2$	80·01	80·18	5·73	5·99	6·22	6·45

[a] A, Benzene; B, pet. ether (b.p. 60–80°); C, benzene–pet. ether (b.p. 80–100°); D, alcohol.
[b] All m.ps are uncorrected.

EXPERIMENTAL

Mannich reaction with 1,2,3-*trione*-2-*arylhydrazones* (IV–VI)

General procedure. To a suspension of the appropriate arylhydrazone (IV–V; 0·01 mole) and piperdine (0·02 mole) in methanol (50 ml), aqueous formaldehyde (35%, 2·5 ml) was added. The reaction mixture was kept overnight at room temp. The solid product was crystallized from alcohol.

The Mannich-bases, VIIa–d and VIIe–h, listed in Table 1, are pale yellow to yellow in colour, insoluble in NaOHaq, give no colour with alcoholic $FeCl_3$, and develop a reddish colour with conc. H_2SO_4.

Compound IVa (0·01 mole) was recovered quantitatively after refluxing its methanolic solution with piperidine (3·0 ml), or with aqueous formaldehyde (35%, 4 ml) in the presence or absence of tri-n-propylamine (1 ml), for 6 hr.

An authentic sample of VIIa was obtained in 85% yield, upon treatment of pyruvaldehyde-1-phenylhydrazone with piperidine and formaldehyde as described above. Identity was proved by m.p. and mixed m.p. determinations.

Compounds VIa–d were recovered, almost quantitatively, upon treatment with piperidine and formaldehyde as described above, after 3 days at room temp and/or after refluxing for 10 hr.

Hydrazones of Mannich-gases (VIIa, b, d)

A suspension of the appropriate Mannich-base (VIIa, b, or d; 0·5 g) and hydrazine hydrate (1 ml) in ethanol (30 ml) was refluxed for 2 hr, left to cool, and diluted with water. The product was crystallized from ethanol.

The hydrazone of 1-N-piperidinomethylpyruvaldehyde-1-phenylhydrazone formed yellow needles m.p. 110°, yield, 61%. (Found: C, 66·21; H, 8·55; N, 25·30. $C_{15}H_{23}N_5$ requires: C, 65·93; H, 8·42; N, 25·64%).

The hydrazone of 1-N-piperidinomethylpyruvaldehyde-1-*o*-totylhydrazone formed yellow needles, m.p. 114°, yield, 65%. (Found: C, 66·72; H, 8·54; N, 24·11. $C_{16}H_{25}N_5$ requires: C, 66·90; H, 8·71; N, 24·39%).

The hydrazone of 1-N-piperidinomethylpyruvaldehyde-1-*p*-tolylhydrazone formed yellow needles m.p. 99°, yield, 59%. (Found: C, 66·61; H, 8·70; N, 24·52. $C_{16}H_{25}N_5$ requires: C, 66·90; H, 8·71; N, 24·39%).

Oximes of Mannich-bases (VIIa, b, d)

Hydroxylamine hydrochloride (1·0 g) was neutralized with NaOHaq and then added to a suspension of the appropriate Mannich-base (VIIa, b, or d; 0·5 g) in ethanol (30 ml). The mixture was refluxed 3 hr, diluted with water, and the product crystallized from ethanol.

The oxime of 1-N-piperidinomethylpyruvaldehyde-1-phenylhydrazone formed yellow needles, m.p. 136°, yield, 56%. (Found: C, 65·48; H, 7·91; N, 20·22. $C_{15}H_{22}ON_4$ requires: C, 65·69; H, 8·03; N, 20·44%).

The oxime of 1-N-piperidinomethylpyruvaldehyde-1-*o*-tolyhydrazone formed yellow needles m.p. 152°, yield, 60%. (Found: C, 66·42; H, 8·35; N, 19·28. $C_{16}H_{24}ON_4$ requires: C, 66·67; H, 8·33; N, 19·44%).

The oxime of 1-N-piperidinomethylpyruvaldehyde-1-*p*-tolyhydrazone formed yellow needles m.p. 154°, yield, 59%. (Found: C, 66·67; H, 8·31; N, 19·54. $C_{16}H_{24}ON_4$ requires: C, 66·67; H, 8·33; N, 19·44%).

Action of aromatic thiols on Mannich-bases (VIIa, d, g, h)

General procedure. A mixture of the appropriate Mannich-base (VIIa, d, g, h; 0·001 mole) and the aromatic thiol (0·003 mole) was heated on a boiling water-bath for 3 hr. The oily residue was triturated with cold dil. alcohol, and the resulting solid crystallized from alcohol.

Compounds VIIIa–b and VIIIc–g, listed in Table 2, are yellow in colour, insoluble in NaOHaq and give red colour with conc. H_2SO_4.

Reaction of 1,2,3-*trione*-2-*arylhydrazones* (IV–VI) *with Grignard reagents*

General procedure. To a cooled Grignard solution (prepared from 1·0 g Mg and the proper quantity of the aryl halide in 100 ml dry ether) was added a suspension of each of the arylhydrazones

(IV–VI; 2·0 g) in dry ether (100 ml). The reaction mixture was kept at room temp for 2 hr, and then decomposed with cold NH_4Claq. The oily residue, obtained upon evaporation of the ethereal layer, was washed several times with pet. ether (b.p. 40–60°), and the resulting solid was crystallized from an appropriate solvent. The Grignard products (Xa–k), listed in Table 3, are pale yellow to yellow in colour, insoluble in NaOHaq, give no colour with alcoholic $FeCl_3$ or copper acetate, and develop a red colour with conc. H_2SO_4.

Action of chromic acid on Xa, b, d

A suspension of the Grignard product (Xa, b, or d; 0·25 g) and chromic acid (0·5 g) in glacial acetic acid (30 ml) was heated on a boiling water-bath for 3 hr, poured into ice-cold water, and extracted with ether. The oily residue, obtained upon evaporation of the ether, was treated with 2,4-dinitrophenylhydrazine. The resulting product proved (m.p. and mixed m.p.) to be acetophenone 2,4 dinitrophenylhydrazone, in the case of Xa and Xb, and to be benzophenone 2,4-dinitrophenylhydrazone in the case of Xd.

Action of hydrazine hydrate on Xh, j, k

To a suspension of the Grignard product (Xh or j; 0·5 g) in ethanol (50 ml), hydrazine hydrate (100%, 2 ml) was added, and the mixture refluxed for 6 hr. The solid, obtained upon dilution of the reaction mixture, was crystallized from benzene–pet. ether (B.p. 60–80°).

The hydrazone of XIa formed pale yellow prisms, m.p. 137°, yield, 53%. (Found: C, 71·59; H, 6·34; N, 22·06. $C_{15}H_{16}N_4$ requires: C, 71·43; H, 6·35; N, 22·22%).

The hydrazone of XIb formed pale yellow prisms, m.p. 157°, yield, 57%. (Found: C, 71·21; H, 6·50; N, 22·49. $C_{15}H_{16}H_4$ requires: C, 71·43; H, 6·35; N, 22·22%).

The hydrazones (XIa–b) are insoluble in NaOHaq and give a red colour with alcoholic $FeCl_3$ and with conc. H_2SO_4.

Compound XIb was also obtained in 51% yield, upon treatment of the Grignard product (Xk) with hydrazine hydrate as described above.

The IR measurements were carried out using a Perkin-Elmer Infracord, Model 137B, in nujol.