BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (10), 2881—2882 (1976)

Oxidation of Flavanone Hydrazones with Manganese Dioxide

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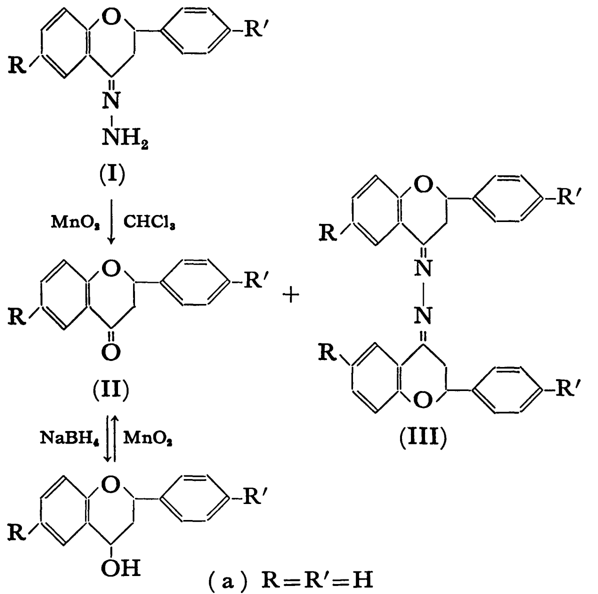
(Received January 27, 1976)

Synopsis. Oxidation of flavanone hydrazones(I) with active manganese dioxide gave a mixture of flavanones(II) and the azines(III).

The oxidation of hydrazones with manganese dioxide has been studied by many workers.[1–8] Scrutiny of literature shows that manganese dioxide oxidation of hydrazones gives different types of products depending upon the reaction conditions and the structure of the parent carbonyl compound. In the present investigations, we have examined the oxidation of flavanone hydrazones with manganese dioxide.

We found that when flavanone hydrazones(I) are shaken with manganese dioxide in chloroform at room temperature, a mixture of the parent ketone(II) and the corresponding azine(III) results in each case.

The identity of the ketones was confirmed by means of melting point and the mixture melting point with authentic samples. Azines were characterized from their elemental analysis and infrared spectra; azines show a strong absorption peak in the region 1605—1610 cm^{-1} due to the conjugated C=N stretching frequency.



(I)

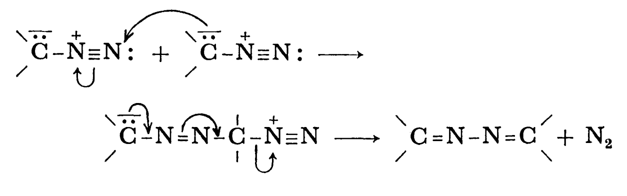
(II)

(III)

(IV)

(a) R=R′=H
(b) R=H, R′=OCH_3
(c) R=CH_3, R′=H
(d) R=CH_3, R′=OCH_3

Maier and Heep[8] oxidized some hydrazones with manganese dioxide to the carbonyl compounds and suggested that diazoalkanes are the intermediates in these reactions. Thus, the formation of flavanone azines can be explained if it is assumed that the intermediate diazo compounds dimerize followed by the loss of nitrogen (Scheme 1).



Scheme 1.

However, the conversion of the hydrazones into flavanones can also be explained by a free radical mechanism* (Scheme 2).

Experimental

All mps are uncorrected.

Flavanone Hydrazones (I). These compounds were synthesized following the reported procedure.[10]

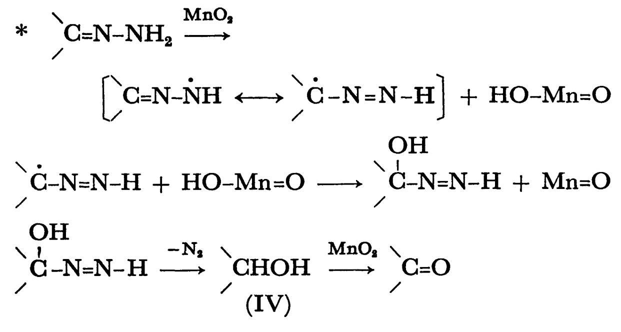
Oxidation of Flavanone Hydrazone (Ia). A mixture of flavanone hydrazone (2 g) and manganese dioxide (10 g) in chloroform (160 ml) was shaken at room temperature for 6 h. The residue, obtained after removal of solvent and manganese dioxide, on fractional crystallization from a mixture of benzene and chloroform gave azine (IIIa) as yellow needles (0.45 g), mp 256—257 °C (lit[10] 254—260 °C). Found: C, 80.4; H, 5.8; N, 6.7%. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.0; H, 5.4; N, 6.3%.

The IR spectrum (KBr) of this azine has absorption bands at 1617, 1607, 1523, 1460, 1380, 1320, 1238, 1220, 1150, 1115, 1070, 1027, 990, 907, 752, and 700 cm^{-1}.

From the mother liquor, flavanone (0.2 g) was also isolated which melted at 76 °C. Mixture melting point with an authentic sample gave no depression.

The oxidation of other flavanone hydrazones was similarly studied. Data for the new compounds are given in Table 1.

Oxidation of Flavan-4-ol (IVa). A mixture of flavan-4-ol



$$* \; {>}C{=}N{-}NH_2 \xrightarrow{MnO_2}$$

$$\left[{>}C{=}N{-}\dot{N}H \longleftrightarrow {>}\dot{C}{-}N{=}N{-}H\right] + HO{-}Mn{=}O$$

$${>}\dot{C}{-}N{=}N{-}H + HO{-}Mn{=}O \longrightarrow {>}\overset{OH}{\overset{|}{C}}{-}N{=}N{-}H + Mn{=}O$$

$${>}\overset{OH}{\overset{|}{C}}{-}N{=}N{-}H \xrightarrow{-N_2} \underset{(IV)}{{>}CHOH} \xrightarrow{MnO_2} {>}C{=}O$$

Scheme 2.

We propose this scheme since compounds containing C–N=N–H are usually unstable and decompose to C–H+N_2, possibly *via* a free radical mechanism. The proposed intermediates flavan-4-ols (IV), however, could not be isolated from the reaction mixture but we found that flavan-4-ols undergo oxidation to the corresponding flavanones under similar reaction conditions. The free radical mechanism was also suggested earlier[9] for the oxidation reactions of diamines, hydrazines and phenylhydrazones with manganese dioxide.

TABLE 1. DATA FOR THE NEW COMPOUNDS

Compd No.	Formula	Mp °C	Solvent of crystallization	Yield (%)	Found (%) Required (%)		
					C	H	N
Ib	$C_{16}H_{16}N_2O_2$	138—139	EtOH	48	—	—	10.2
					—	—	10.4
Ic	$C_{16}H_{16}N_2O_2$	129—130	EtOH	50	—	—	11.0
					—	—	11.1
Id	$C_{17}H_{18}H_2O_2$	130—131	EtOH	45	—	—	9.7
					—	—	9.9
IIIb	$C_{32}H_{28}N_2O_4$	254—255	C_6H_6-$CHCl_3$	20	76.2	5.8	5.7
					76.1	5.5	5.5
IIIc	$C_{32}H_{28}N_2O_2$	242—243	C_6H_6-$CHCl_3$	18	81.4	6.2	6.3
					81.3	5.9	6.8
IIId	$C_{32}H_{32}N_2O_4$	252—253	C_6H_6-$CHCl_3$	19	76.5	5.8	5.4
					76.7	6.0	5.3
IVc	$C_{16}H_{16}O_2$	127—128	EtOH-H_2O	80	79.8	6.5	—
					80.0	6.6	—

(2 g) and manganese dioxide (10 g) in chloroform was shaken for 6 h. The reaction mixture was worked up as usual to afford flavanone (1.2g), mp and mmp 76 °C.

The other flavan-4-ols[11,12] when oxidized similarly gave the corresponding flavanones in 50—55% yield.

The authors thank Professor M. M. Bokadia for providing laboratory facilities and to the authorities of Chemistry Department I. I. T. Kanpur for providing analytical and spectral data. One of us (V. S.) is grateful to U. G. C., New Delhi for the award of a research fellowship.

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