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Manganic Acetate Oxidation of 2′-Hydroxychalcones

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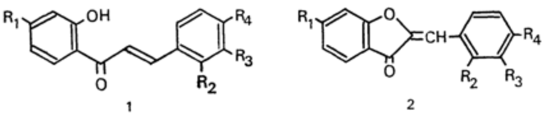
Although manganic acetate has received less attention than lead tetraacetate, several oxidation reactions of phenols,[1] ketones,[2] aromatic hydrocarbons,[3] and phenyl ethers[4] by a reagent have been reported recently. During my investigation of the oxidation of various organic compounds, it was demonstrated that manganic acetate reacted with 2′-hydroxychalcones in acetic acid to give aurones in fairly good yield. Aurones have so far been prepared either by dehydrobromination of dibromochalcones or by the condensation of 3-benzofuranones with benzaldehydes. This oxidation of 2′-hydroxychalcones gave an alternative way to make aurones.



1 2

a $R_1=R_2=R_3=H$, $R_4=OCH_3$
b $R_1=R_2=H$, $R_3, R_4=OCH_2O$
c $R_1=R_3=H$, $R_2=R_4=OCH_3$
d $R_1=H$, $R_2=R_3=R_4=OCH_3$
e $R_1=R_4=OCH_3$, $R_2=R_3=H$
f $R_1=OCH_3$, $R_2=H$, $R_3, R_4=OCH_2O$
g $R_2=H$, $R_1=R_3=R_4=OCH_3$
h $R_3=H$, $R_1=R_2=R_4=OCH_3$
i $R_1=R_2=R_3=R_4=OCH_3$

Fig. 1

A mixture of a chalcone (1 mmol) and manganic acetate (2 mmol) was heated in acetic acid at 100°C for a period of 10 to 30 min. The reaction mixture was hydrolysed with water, extracted with chloroform, and separated on silica gel plates.

An appropriate band on the plates was scraped out and then extracted again with chloroform. Recrystallization from ethanol gave pure aurone

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[1] R. van Helden, A. F. Bickel and E. C. Kooyman, *Rec. Trav. Chim.*, **80**, 1237 (1961); *Chem. Abstr.*, **56**, 10026d (1961).

[2] R. van Helden and E. C. Kooyman, *ibid.*, **80**, 57 (1961); *Chem. Abstr.*, **55**, 17565a (1961).

[3] S. A. Zonis, *Sbornik Statei Obshchei Khim.*, **2**, 109 (1953); *Chem. Abstr.*, **49**, 5414 (1955).

[4] T. Aratani and M. J. S. Dewer, *J. Am. Chem. Soc.*, **88**, 5479 (1966).

Table 1

Chalcone				Aurone						
No.	Mp (°C)	Lit. mp	Ref.	No.	Reaction time (min)	Yield (%)	IR $\nu_{max}^{CHCl_3}$ (cm^{-1})	Mp (°C)	Lit. mp	Ref.
1a	93	93—94	5)	2a	14	29	1700, 1640, 1590	137	137—139	13)
1b	138	137—138	6)	2b	30	18	1700, 1640, 1605, 1590	190	192	6)
1c	111	107	7)	2c	20	52	1700, 1640, 1610, 1588	182	182—183	14)
1d	78	77—78	8)	2d	30	38	1700, 1640, 1584	145*	—	
1e	115	113—114	9)	2e	22	34	1700, 1644, 1600	133	134	15)
1f	148	148.5	10)	2f	10	23	1700, 1644, 1610, 1596	178	175	10)
1g	157	156—157	11)	2g	40	40	1700, 1644, 1610, 1592	186	189	16)
1h	156	157	12)	2h	8	59	1700, 1640, 1590	184*	—	
1i	147*	—		2i	30	45	1700, 1642, 1605, 1587	129*	—	

* Elemental analysis gave a satisfactory agreement with the calculated value.

which was identified with its melting point and IR spectrum (ν_{max} 1700 cm^{-1}, a characteristic carbonyl band of 3-benzofuranone), compared with those of an authentic sample. The resultes are shown in Table 1.

A chalcone having hydroxyl group other than at 2′-position was also subjected to oxidation. However, this resulted in a variety of products, none of which was isolated as a pure crystalline form.

The reaction mechanism could be written similarly to the reaction of lead tetraacetate with phenols. The first step in the reaction is the formation of Ar–O–Mn(OAc)$_2$ group.17) Homolysis of O–Mn bond gives a radical, Ar–$\dot{\text{O}}$, and manganese diacetate as shown in Fig. 2. Heterolysis of the bond is unlikely to occur as manganic acetate is one electron oxidizing reagent. Then, the radical attacks C–H bonds in suitable spatial position,18) which is α-hydrogen in this case, to give aurone (2). Further studies on solvent effects and temperature dependence of the reaction are now in progress.

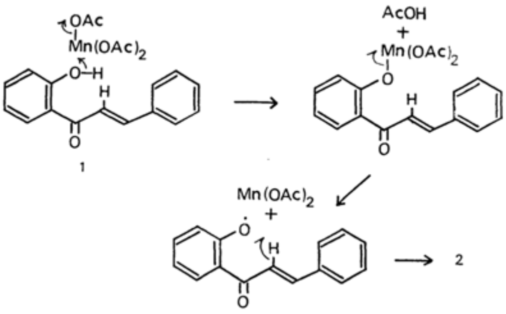

Fig. 2

Experimental

Measurements. Melting points were determined with Mitamura Melting Point Measuring Apparatus. The IR spectra were obtained with a Shimadzu IR spectrometer in chloroform.

Chalcones. One equivalent each of 2′-hydroxyacetophenone and benzaldehyde was dissolved in a small volume of ethanol and the solution was treated with 50% aqueous potassium hydroxide with stirring. The mixture was poured into cold dilute hydrochloric acid. The precipitates were collected by filtration and recrystallized from ethanol.

Manganic Acetate. Manganic acetate was prepared according to Dewer's method.4)

Manganic Acetate Oxidation of Chalcones. A chalcone (1 mmol), dissolved in acetic acid (15 m*l*) was heated with manganic acetate (2 mmol) at 100°C

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5) F. Herstein and St. v. Kostanecki, *Ber.*, **32**, 318 (1899).

6) W. Feuerstein and St. v. Kostanecki, *ibid.*, **32**, 315 (1899).

7) S. Hattori, *Acta Phytochem. Tokyo*, **6**, 152 (1932); *Chem. Abstr.*, **26**, 4816 (1932).

8) W. D. Ollis and K. Kurosawa, unpublished result.

9) St. v. Kostanecki and F. W. Osius, *Ber.*, **32**, 322 (1899).

10) T. Emilewicz. and St.v Kostanecki, *ibid.*, **32**, 313 (1899).

11) St. v. Kostanecki and S. Nikowski, *ibid.*, **38**, 3587 (1905).

12) St. v. Kostanecki, V. Lampe and S. Triulzi, *ibid.*, **39**, 92 (1906).

13) B. I. Nurunnabi, *Pakistan J. Sci. Ind. Research*, **4**, 34 (1961).

14) J. Tambor and H. Gubler, *Helv. Chim. Acta*, **2**, 110 (1918).

15) Y. Okajima, *Yakugaku Zasshi*, **80**, 318 (1960); *Chem. Abstr.*, **54**, 18488f (1960).

16) A. Blom and J. Tambor, *Ber.*, **38**, 3590 (1905).

17) W. A. Waters and J. S. Littler, "Oxidation in Organic Chemistry," ed. by K. B. Wiberg, Academic Press Inc., New York, N. Y. and London (1965), p. 226.

18) F. F. Stephens and J. D. Bower, *J. Chem. Soc.*, **1949**, 2971.

until a dark solution turned into clear orange. After removal of the acetic acid *in vacuo*, the resulting solid was treated with water (10 m*l*) and then extracted with chloroform (20 m*l*). The chloroform layer was separated from aqueous solution and evaporated. The residue was dissolved in a small amount of chloroform and separated on silica gel plates (Wako gel B, 10 g × 5) with chloroform as an eluant. A yellow band running below the unchanged chalcone was scraped out and extracted with chloroform. The chloroform was distilled off and the crude aurone was recrystallized from ethanol.

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