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STUDIES ON THE PREPARATION AND PROPERTIES OF SOME PHENOLIC AND CARBOXYLIC DERIVATIVES OF DICYCLOOCTATETRAENYLMOLYBDENUM OXIDE DICHLORIDE

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SUMMARY

Reactions of dicyclooctatetraenylmolybdenum oxide dichloride, $(C_8H_7)_2MoOCl_2$ (I) with mono-, di-, and trihydroxyphenols and with mono- and dicarboxylic acids have been studied, and phenoxide and carboxylate derivatives of (I) have been isolated. In these compounds the chlorine atoms of (I) are replaced by phenoxide or carboxylate groups. IR spectra and some other physical characteristics of all the compounds are reported.

INTRODUCTION

In a previous communication we reported[1] an interesting cyclooctatetraenyl compound of molybdenum, $(C_8H_7)_2MoOCl_2$ (I), in which cyclooctatetraene is present as cyclooctatetraenyl anion. This paper deals with the reactions of (I) with mono-, di- and trihydroxyphenols and also with mono- and di-carboxylic acids.

EXPERIMENTAL

Special precautions were taken to exclude moisture. Benzene dried with and distilled over sodium was further purified by azeotropic distillation with ethyl alcohol. Freshly distilled purum cyclooctatetraene (Fluka, AG, Buchs), phenol, cresols, formic, acetic, propionic and butyric acids were used, and the remaining phenols and carboxylic acids were recrystallised before use. Molybdenum oxide tetrachloride, $MoOCl_4$, was prepared by the method reported by Colton *et al.*[2]. Dicyclooctatetraenylmolybdenum oxide dichloride, $(C_8H_7)_2MoOCl_2$ (I) was prepared by the method reported by Jain *et al.*[1]. IR spectra (in KBr) of the compound were recorded on a Perkin–Elmer Model 137 spectrophotometer.

Preparation of dicyclooctatetraenyldiphenoxymolybdenum oxide

To 1.25 g of (I) in 100 ml of dry benzene was added 0.61 g of freshly distilled phenol, and the reaction mixture was refluxed. Evolution of hydrogen chloride gas began after $\frac{1}{2}$ h, and refluxing was continued until the evolution of this gas had ceased

TABLE 1

DETAILS OF THE PREPARATION, PROPERTIES AND ANALYSIS OF PHENOXIDE DERIVATIVES OF $(C_8H_7)_2MoOCl_2$

Compound	$(C_8H_7)_2MoOCl_2$ taken (g)	Corresponding phenol added (g)	Benzene added (ml)	Reaction time (h)	Colour	Yield (%)	Analytical data (%)		
							Mo found (calcd.)	C found (calcd.)	H found (calcd.)
$(C_8H_7)_2MoO(OC_{10}H_7)_2$	1.25	1-Naphthol 0.92	100	40	Greenish blue	91	15.75 (15.89)	71.29 (71.55)	4.62 (4.64)
$(C_8H_7)_2MoO(OC_{10}H_7)_2$	1.65	2-Naphthol 1.22	150	50	Blue	90	15.85 (15.89)	71.35 (71.55)	4.60 (4.64)
$(C_8H_7)_2MoO(OC_6H_4.CH_3)_2$	1.50	*o*-Cresol 0.83	80	45	Greenish black	96	18.00 (18.04)	67.65 (67.69)	5.22 (5.26)
$(C_8H_7)_2MoO(OC_6H_4.CH_3)_2$	1.84	*m*-Cresol 1.02	100	55	Greenish black	94	18.00 (18.04)	67.69 (67.69)	5.25 (5.26)
$(C_8H_7)_2MoO(OC_6H_4.CH_3)_2$	2.16	*p*-Cresol 1.20	200	62	Greenish black	92	18.04 (18.04)	67.66 (67.69)	5.23 (5.26)
$(C_8H_7)_2MoO(O_2C_6H_4)$	1.45	Catechol 0.41	100	42	Shining black	97	22.50 (22.53)	61.90 (61.98)	4.20 (4.23)
$(C_8H_7)_2MoO(O_2C_6H_4)$	2.45	Resorcinol 0.89	200	70	Black	93	22.30 (22.53)	61.95 (61.98)	4.15 (4.23)
$C_8H_7)_2MoO(O_2C_6H_4)$	2.05	Hydroquinone 0.58	150	58	Brownish black		22.50 (22.53)	61.90 (61.98)	4.18 (4.23)
$(C_8H_7)_2MoO(O_3C_6H_4)$	1.82	Pyrogallol 0.59	150	55	Bluish black	92	21.52 (21.71)	59.70 (59.74)	4.00 (4.07)
$(C_8H_7)_2MoO(O_3C_6H_4)$	2.10	Phloroglucinol 0.68	100	62	Black	90	21.65 (21.71)	59.70 (59.74)	3.95 (4.07)

(38 h). The mixture was cooled to room temperature and the dark blue solution was evaporated to dryness under reduced pressure. The residue was repeatedly washed with ethyl alcohol and dried to give a dark blue crystalline compound (yield 96%) whose analysis corresponded to $(C_8H_7)_2MoO\,(OC_6H_5)_2$. (Found: C, 66.50; H, 4.70; Mo, 18.85. $C_{28}H_{24}MoO_3$ calcd.: C, 66.67; H, 4.76; Mo, 19.04%.)

Other phenoxy derivatives of (I) were prepared similarly and the data regarding their preparation, properties and analysis are given in Table 1. IR spectra (cm^{-1}) of the phenoxy derivatives of (I) in KBr have been recorded and the various peaks for $(C_8H_7)_2\,MoO(OC_6H_5)_2$ are given below: 690 w, 750 m, 812 w, 910 w, 975 s, 1020 w, 1220 m, 1400 w, 1475 w, 1500 w, 1600 s, 3000 m.

Preparation of dicyclooctatetraenyldiacetatomolybdenum oxide

To 1.95 g of (I) in 150 ml of dry benzene added 0.62 g of acetic acid and refluxed the contents. The evolution of hydrogen chloride gas started immediately on refluxing and the refluxing was continued till the evolution of hydrogen chloride gas ceased (55 h). The contents were cooled to room temperature and then dried under reduced pressure. The resultant compounds were washed with ethyl alcohol and dried when a bluish-black crystalline compound (yield 95%) was obtained, the composition of which corresponded to the formula, $(C_8H_7)_2MoO(O_2CCH_3)_2$. (Found: C, 54.75; H, 4.55; Mo, 21.80. $C_{20}H_{20}MoO_5$ calcd.: C,.55.05; H, 4.59; Mo, 22.01%.)

Reactions of (I) with other carboxylic acids were carried out in a similar manner and the data in connection with their preparation, properties and analysis is given in Table 2. IR spectra (cm^{-1}) of the carboxylates of (I) in KBr have been recorded and various peaks for $(C_8H_7)_2MoO(CH_3COO)_2$ are given below: 690 w, 752 w, 910 m, 980 s, 1030 w, 1110 w, 1310 m, 1400 s, 1450 m, 1615 s, 1720 m, 3005 m.

RESULTS AND DISCUSSION

Phenoxide derivatives

The composition of the phenoxide derivatives of (I) suggests that in the case of monohydroxyphenols, one mole of (I) reacts with two moles of the phenols, whereas in case of di- and trihydroxyphenols only one mole of these phenols combine with one mole of (I). The formation of the derivatives can be represented by the following general equation:

$$(C_8H_7)_2MoOCl_2+n\text{ P} \rightarrow (C_8H_7)_2MoO(\text{P}-x\text{ H})_n+n\cdot x\text{ HCl}$$

where P = corresponding phenol
$x=1, n=2$; for monohydroxyphenols
$x=2, n=1$; for di- and trihydroxyphenols

IR spectra of phenoxide derivatives of (I)

The IR spectra of the compounds were recorded in the region 4000–670 cm^{-1}. The bands of medium intensity at ~3000 cm^{-1} can be assigned to C–H stretching frequency and those at ~1600 cm^{-1} may be due to C=C stretching. The bands at ~690 cm^{-1}, at ~1400 cm^{-1} and at ~1450 cm^{-1} are due to ring distortion of cyclooctatetraene[3] and C–C stretching is associated with the bands at ~900 cm^{-1}. The additional bands at ~1350 cm^{-1} in the case of *o*-, *m*-, *p*-cresol derivatives are due to $-C-CH_3$ vibrations[4]. In the case of pyrogallol and phloroglucinol compounds out of

TABLE 2

DETAILS OF THE PREPARATION, PROPERTIES AND ANALYSIS OF CARBOXYLATE DERIVATIVIS OF $(C_8H_7)_2MoOCl_2$

Compound	$(C_8H_7)_2MoOCl_2$ taken (g)	Correspond-ing carboxylic acid added (g)	C_6H_6 added (ml)	Reaction time (h)	Colour	Yield (%)	Analytical data (%)		
							Mo found (calcd.)	C found (calcd.)	H found (calcd.)
$(C_8H_7)_2MoO(O_2CH)_2$	1.80	Formic 0.43	140	55	Green	95	23.50 (23.53)	52.93 (52.97)	3.85 (3.92)
$(C_8H_7)_2MoO(O_2CC_2H_3)_2$	1.56	Proprionic 0.60	120	45	Bluish green	94	20.66 (20.68)	56.90 (56.93)	5.00 (5.18)
$(C_8H_7)_2MoO(O_2CC_3H_7)_2$	1.88	Butyric 0.85	150	58	Greenish black	94	19.50 (19.50)	58.54 (58.55)	5.65 (5.69)
$(C_8H_7)_2MoO\begin{bmatrix}OOC\\ \vert\\ OOC\end{bmatrix}$	2.00	Oxalic 0.47	160	60	Dark brown	92	23.65 (23.63)	53.00 (53.22)	3.40 (3.45)
$(C_8H_7)_2MoO\left[CH_2\begin{matrix}\diagup COO\\ \diagdown COO\end{matrix}\right]$	1.95	Malonic 0.53	150	60	Brownish black	92	22.82 (22.85)	54.31 (54.30)	3.75 (3.81)
$(C_8H_7)_2MoO\begin{bmatrix}CH_2COO\\ \vert\\ CH_2COO\end{bmatrix}$	1.52	Succinic 0.47	100	42	Black	90	22.00 (22.11)	53.22 (53.31)	4.21 (4.15)
$(C_8H_7)_2MoO(O_2CC_6H_5)_2$	1.85	Benzoic 1.16	150	56	Black	90	17.00 (17.14)	64.27 (64.30)	4.25 (4.29)

the three hydrogen atoms of the hydroxyl groups present in these phenols, only two hydrogen atoms are replaced, as is confirmed by the IR spectra of the derivatives, which show strong bands at ~3600 cm^{-1} due to the presence of free –OH groups (phenolic)[5–7]; these bands are absent in all other phenoxy derivatives. This observation is further confirmed by the presence of bands at ~1180 cm^{-1} which are due to –OH deformation[8]. The bands at ~980 cm^{-1}, at ~750 cm^{-1} and ~1410 cm^{-1} are due to M=O[9], M–C_8H_7 linkage[1,3] and M–O–C stretching frequencies[10–12] respectively.

Carboxylate derivatives

The compositions of the carboxylates of (I) indicate that in the case of monocarboxylic acids one mole of (I) reacts with two moles of the acid, whereas in the case of dicarboxylic acids only one mole of the acid reacts with one mole of (I). The formation of the carboxylates of (I) can be represented by the following general equation.

$$(C_8H_7)_2MoOCl_2 + n\,A \rightarrow (C_8H_7)_2MoO(A - x\,H)_n + n \cdot x\,HCl$$

where A = corresponding acid
$x = 1, n = 2$, for monocarboxylic acids
and $x = 2, n = 1$, for dicarboxylic acids

IR spectra of the carboxylates of (*I*) *in the range* 4000–670 *cm^{-1}*. The C=O stretching vibrations[13–15] in all the carboxylates except the benzoic acid derivative appear at ~1715 cm^{-1}; this vibration[16] in the benzoic acid derivative appears at ~1690 cm^{-1}. The bands at ~1350 cm^{-1} in the case of propionic and butyric acid derivatives are due to the presence of –C–CH_3 stretching vibrations[17], and these bands are absent in all other cases. The bands at ~3000 cm^{-1} can be assigned to the C–H stretching frequency. C=C stretching and C–C stretching frequencies are associated with bands at ~1600 cm^{-1} and at ~900 cm^{-1} respectively. The bands at ~690 cm^{-1}, at ~1400 cm^{-1} and at ~1450 cm^{-1} are due to ring distortion of cyclooctatetraene[3]. The C–O–M bond in all the compounds gives rise to a band at ~1300 cm^{-1}. The extra bands in the case of propionic and butyric acid derivatives at ~1410 cm^{-1} are due to the presence of the CH_2 group adjacent to a C=O group[18–20]. The bands at ~980 cm^{-1} and at ~750 cm^{-1} are associated with M=O[9] and M–C_8H_7 linkages[1,3] respectively.

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