

Synthesis of η^6 -(Heteroarene)tricarbonylchromium Complexes under Ethyl Formate Catalysis

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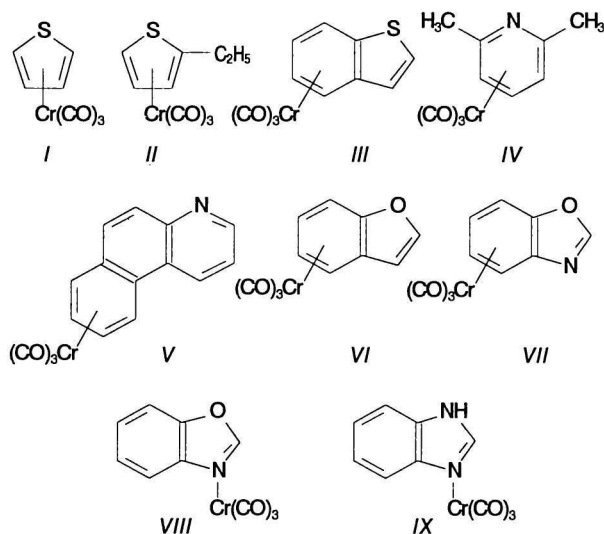
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The direct complexation of eight various heterocycles with $\text{Cr}(\text{CO})_6$ under ethyl formate catalysis was studied. Higher or comparable yields of complexes were reached in less than 4.25 h time in comparison with published uncatalyzed procedures which need long reaction time. This method failed in the case of *N*-methylpyrrole, furan, and 4-amino-2-methylquinoline. When benzoxazole and benzimidazole were complexed, the main products did not have the desired structure.

In our previous works [1–3] we found that the esters are good catalysts for the complexation of different benzene derivatives with $\text{Cr}(\text{CO})_6$ in boiling decalin. The main goal of this work was to find out if this method could be used for the synthesis of η^6 -(heteroarene) $\text{Cr}(\text{CO})_3$ complexes.

The preliminary experiments proved that the ethyl formate is better catalyst than butyl acetate at the complexation of heteroarenes with $\text{Cr}(\text{CO})_6$. Formulae of the obtained complexes are presented in Scheme 1 and the results are summarized in Table 1.



Scheme 1

Table 1. Results of Complexation of Heteroarenes with $\text{Cr}(\text{CO})_6$ in Boiling Decalin in the Presence of Ethyl Formate

Entry	Reaction time/h	Product	Yield/%
1	4.25	I	13.8
2	4.25	II	25.0
2a	6.50	II	39.0
3	3.75	III	31.0
4	3.25	IV	14.0
5	2.00	V	39.0
6	2.00	VI	12.0
7	1.00	VII	0.7
		VIII	18.0
8	0.50	IX	19.6

plex was increased using longer reaction time (Table 1, entry 2a). Repeating of experiments showed good reproducibility of our results, e.g. product I was obtained in 13.8–15.8 % yield during 4.25–5.75 h and product II in 21–39 % yield during 4.0–6.5 h. Our method gave good result at complexation of thianaphthene (31 %) while King and Stone [7] prepared the same complex in 2 % yield and Fischer *et al.* [8] by 20 h heating of the ligand with $\text{Cr}(\text{CO})_6$ in dibutyl ether–*n*-heptane mixture in 22 % yield.

η^6 -(2,6-Dimethylpyridine)tricarbonylchromium was prepared in 14 % yield after 3.25 h by our method but in 30 % yield by 36 h heating of the reactant in refluxing dioxane [9]. The complexation of benzo-[f]quinoline under ethyl formate catalysis is better method for preparation of desired product (39 %, 2 h) than the synthesis of the same complex described in [8] (8 %, 4 h).

Catalyzed complexation gave just 12 % yield of benzofuran complex after 2 h heating in refluxing decalin while 37 % yield of η^6 -(benzofuran)tricarbonylchromium was achieved by 12 h reflux of components in dibutyl ether [8].

We failed at the attempts at complexation of furan and *N*-methylpyrrole in spite of the fact that η^6 -(*N*-methylpyrrole)tricarbonylchromium was prepared in 46 % yield by heating $\text{Cr}(\text{CO})_6$ with 20 mol excess

From the data collected in Table 1 it follows that our method gave higher yields in shorter reaction time of η^6 -(thiophene)tricarbonylchromium (13.8 %) than direct complexation of thiophene in boiling dibutyl ether (2.6–3.4 %) [4]. But it should be noted that this complex could be prepared in 40 % or 86 % yield using $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$ [5] or $\text{Cr}(\text{CO})_3(\text{Py})_3$ [6] as the complexation agents. Even higher yield (25.0 %) was obtained at complexation of 2-ethylthiophene (not described in literature). The yield of this com-

of *N*-methylpyrrole or in 76 % yield using $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ as the complexation agent [10]. During the heating of 4-amino-2-methylquinoline with $\text{Cr}(\text{CO})_6$ and ethyl formate in boiling decalin a red solid material was separated on the walls of condenser as well as on the reaction flask. Unfortunately, during purification of the supposed product by flash chromatography, a decomposition of the prepared complex started and merely the starting material was recovered.

When the complexations of benzoxazole and benzimidazole were made, we observed that the evolution of CO was very rapid in these cases but the results were not good. The complexation of benzoxazole yielded just 0.7 % of the desired complex VII. The main product was the *N*- $\text{Cr}(\text{CO})_5$ complex, the structure of which was confirmed by mass and IR spectra (see Experimental). The analogous *N*- $\text{Cr}(\text{CO})_5$ complex IX was the only compound which was isolated at the attempt of the complexation of benzimidazole.

EXPERIMENTAL

The apparatus described in [11] was evacuated and filled with argon. Then $\text{Cr}(\text{CO})_6$ (2.3 mmol), ethyl formate (20.7 mmol), heteroarene (6.9 mmol), and decalin (70 cm³) were placed into the flask. The apparatus was again evacuated and filled with inert gas three—four times. The reaction mixture was refluxed until about 120 % of calculated amount of CO was evolved. Then the heating was stopped and the flask with reaction mixture was cooled down. The flash chromatography on silica gel column (40—100 μm , 2.5 cm \times 10 cm) was used as a purification procedure. Decalin was washed down by isohexane while the product was adsorbed on silica gel. Then the complex was eluted by the mixture of ethyl acetate and isohexane ($\phi_r = 1:10$ — $1:3$) or by ethyl acetate. The obtained solution was concentrated under diminished pressure and the pure product was crystallized from the ethyl acetate—iso-hexane mixture. In each experiment, 0.5 g of $\text{Cr}(\text{CO})_6$ was used.

Spectral data and other characteristics follow. ¹H NMR spectra of deuteriochloroform or deuterioacetone solutions were measured with Tesla NMR-587 instrument, tetramethylsilane being the internal reference. The IR spectra were obtained on Perkin—Elmer spectrometer and mass spectra were taken with AET-MS 902 spectrometer at 70 eV energy.

η^6 -(Thiophene) $\text{Cr}(\text{CO})_3$ (I); m.p. = 128—131 °C (decomp.), Ref. [6] gives m.p. = 160 °C (decomp.). For $\text{C}_7\text{H}_4\text{CrO}_3\text{S}$ ($M_r = 220.2$) $w_i(\text{calc.})$: 38.19 % C, 1.83 % H, 14.53 % S; $w_i(\text{found})$: 38.24 % C, 1.83 % H, 12.87 % S. ¹H NMR spectrum (deuteriochloro-

form), δ : 5.59 (t, 2H, H- α_{arom}), 5.35 (t, 2H, H- β_{arom}). η^6 -(2-Ethylthiophene) $\text{Cr}(\text{CO})_3$ (II); m.p. = 75—76 °C. For $\text{C}_9\text{H}_8\text{CrO}_3\text{S}$ ($M_r = 248.2$) $w_i(\text{calc.})$: 43.55 % C, 3.65 % H, 12.92 % S; $w_i(\text{found})$: 43.49 % C, 3.19 % H, 11.38 % S. ¹H NMR spectrum (deuteriochloroform), δ : 5.53 (t, 1H, H- β_{arom}), 5.34 (d, 1H, H- α_{arom}), 5.23 (d, 1H, H- β_{arom}), 2.58 (q, 2H, CH_2CH_3), 1.24 (t, 3H, CH_2CH_3).

η^6 -(Thianaphthene) $\text{Cr}(\text{CO})_3$ (III); m.p. = 128—130 °C (decomp.), Ref. [7] gives m.p. = 115 °C, Ref. [8] gives m.p. = 130—131 °C. For $\text{C}_{11}\text{H}_6\text{CrO}_3\text{S}$ ($M_r = 270.2$) $w_i(\text{calc.})$: 48.89 % C, 2.24 % H, 11.84 % S; $w_i(\text{found})$: 48.44 % C, 2.20 % H, 10.59 % S. ¹H NMR spectrum (deuteriochloroform), δ : 7.44 (d, 1H), 7.08 (dd, 1H), 6.24 (m, 2H), 5.34 (m, 2H, H_{arom}).

η^6 -(2,6-Dimethylpyridine) $\text{Cr}(\text{CO})_3$ (IV); m.p. = 146.5 °C (decomp.). For $\text{C}_{10}\text{H}_9\text{CrNO}_3$ ($M_r = 243.2$) $w_i(\text{calc.})$: 49.39 % C, 3.73 % H, 5.76 % N; $w_i(\text{found})$: 49.14 % C, 3.68 % H, 5.64 % N. ¹H NMR spectrum (deuteriochloroform), δ : 5.66 (t, 1H), 5.12 (d, 2H, H_{arom}), 2.42 (s, 6H, CH_3).

η^6 -(Benzof[*f*]quinoline) $\text{Cr}(\text{CO})_3$ (V); m.p. = 179—181 °C (decomp.). Ref. [8] gives m.p. = 172—175 °C. For $\text{C}_{16}\text{H}_9\text{CrNO}_3$ ($M_r = 315.2$) $w_i(\text{calc.})$: 60.95 % C, 2.88 % H, 4.44 % N; $w_i(\text{found})$: 61.30 % C, 2.90 % H, 4.32 % N. ¹H NMR spectrum (deuteriochloroform), δ : 8.98 (dd, 1H), 8.63 (d, 1H), 7.54—7.91 (m, 3H), 6.56 (m, 1H), 6.06 (m, 1H), 5.53—5.63 (m, 2H, H_{arom}).

η^6 -(Benzofuran) $\text{Cr}(\text{CO})_3$ (VI); m.p. = 126.5 °C, Ref. [8] gives m.p. = 118—119 °C. For $\text{C}_{11}\text{H}_6\text{CrO}_4$ ($M_r = 254.2$) $w_i(\text{calc.})$: 51.98 % C, 2.38 % H; $w_i(\text{found})$: 52.04 % C, 2.31 % H. ¹H NMR spectrum (deuteriochloroform), δ : 7.52 (d, 1H), 6.64 (dd, 1H), 6.16 (d, 1H), 5.40 (dt, 1H), 5.01 (t, 1H, H_{arom}).

η^6 -(Benzoxazole) $\text{Cr}(\text{CO})_3$ (VII); m.p. = 114—116 °C (decomp.). For $\text{C}_{10}\text{H}_5\text{CrNO}_3$ ($M_r = 255.2$) $w_i(\text{calc.})$: 47.07 % C, 1.98 % H, 5.49 % N; $w_i(\text{found})$: 47.24 % C, 1.98 % H, 5.10 % N. ¹H NMR spectrum (deuteriochloroform), δ : 7.94 (s, 1H), 6.38 (d, 1H), 6.20 (d, 1H), 5.33 (t, 1H, H_{arom}).

η^2 -(Benzoxazole) $\text{Cr}(\text{CO})_5$ (VIII); m.p. = 134—137 °C (decomp.). For $\text{C}_{12}\text{H}_5\text{CrNO}_5$ ($M_r = 311.2$) $w_i(\text{calc.})$: 46.32 % C, 1.62 % H, 4.50 % N; $w_i(\text{found})$: 46.09 % C, 1.51 % H, 4.15 % N. IR spectrum, $\tilde{\nu}/\text{cm}^{-1}$: 1945 $\nu(\text{CO})$, 1927 $\nu(\text{CO})$. ¹H NMR spectrum (deuterioacetone), δ : 8.10—8.12 (m, 1H), 7.59—7.92 (m, 4H, H_{arom}). Mass spectrum, m/z : 311 (M^{+}), 199 ($\text{M}^{+} - 4 \text{ CO}$), 119 ($\text{M}^{+} - \text{Cr}(\text{CO})_5$), 91 (C_7H_7^{+}).

η^2 -(Benzimidazole) $\text{Cr}(\text{CO})_5$ (IX); m.p. = 118—127 °C. For $\text{C}_{12}\text{H}_6\text{CrN}_2\text{O}_5$ ($M_r = 310.2$) $w_i(\text{calc.})$: 46.47 % C, 1.95 % H, 9.03 % N; $w_i(\text{found})$: 46.42 % C, 1.85 % H, 8.86 % N. IR spectrum, $\tilde{\nu}/\text{cm}^{-1}$: 1933 $\nu(\text{CO})$, 1913 $\nu(\text{CO})$. ¹H NMR spectrum (deuteriochloroform), δ : 8.11 (s, 1H), 8.02—8.10 (m, 1H), 7.37—7.98 (m, 3H, H_{arom}). Mass spectrum, m/z : 310 (M^{+}), 198 ($\text{M}^{+} - 4 \text{ CO}$), 118 ($\text{M}^{+} - \text{Cr}(\text{CO})_5$), 91 (C_7H_7^{+}).

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Preparation of 5-Substituted 4-Oxo-4H-pyran-2-carbaldehydes and Their Condensation Reactions

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Primary alcohol group oxidation in position 2 of kojic acid molecule (5-hydroxy-2-hydroxymethyl-4H-pyran-4-one) to the corresponding aldehyde is described and a number of condensation reactions of 5-substituted kojic acid aldehyde (comenic aldehyde) with different agents is given.

5-Substituted 4-oxo-4H-pyran-2-carbaldehydes have been prepared *via* several alternative routes. Becker [1, 2] carried out the oxidation of hydroxymethyl group of kojic acid methyl ether by MnO_2 in benzene and in dioxane; Thomas [3] used CHCl_3 and authors in [4] 2-methyl-2-propanol as the solvent.

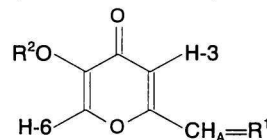
Condensation of *N*-alkylpyridinium salts with *p*-nitrosodimethylaniline (Kröhnke reaction) and following hydrolysis of arising intermediate was used for the synthesis of 5-methoxy-4-oxo-4H-pyran-2-carbaldehyde [5].

Since MnO_2 oxidations lead to yields of 5-substituted comenic aldehydes up to 20 %, the present paper describes use of SeO_2 in xylene for this purpose.

The reactivity of aldehydes prepared by this method was studied in condensation reactions with malonic acid and its derivatives, hydroxylamine, phenylhydrazine, thiosemicarbazide, and some aromatic amines (Table 1, III–XV).

While reactions with hydroxylamine or *o*-phenylenediamine proceeded in ethanol without catalysts, the other condensations required special conditions.

Structures of synthesized compounds



were determined and confirmed by the elemental and the spectral analysis. In selected compounds the confirmation of the structure was also supported by mass spectral analysis data.

IR spectra of the above synthesized kojic acid derivatives yielded stretching vibrations as follows: $\nu(\text{C}=\text{O})$ intense band in the $\tilde{\nu}$ region $1620\text{--}1710\text{ cm}^{-1}$, $\nu(\text{C}-\text{O}-\text{C})$ at $\tilde{\nu} = 1190\text{--}1310\text{ cm}^{-1}$, $\nu(\text{C}=\text{C})$ intense bands at $\tilde{\nu} = 1480\text{--}1590\text{ cm}^{-1}$. Derivative IV (Table 1) exerted a bright band of stretching vibrations $\nu(\text{CN})$ at $\tilde{\nu} = 2220\text{ cm}^{-1}$. Stretching vi-