EXPLORATION OF THE NEW METHOD FOR THE SYNTHESIS OF η6-ARENETRICARBONYLCHROMIUM COMPLEXES. THE SCOPE AND LIMITATIONS

Peter HRNČIAR[a], Milan HUDEČEK[a], Gusein K. I. MAGOMEDOV[b] and Štefan TOMA[a]

[a] *Department of Organic Chemistry,*
Comenius University, 842 15 Bratislava, Czechoslovakia
[b] *State Scientifique — Research Institute of Chemistry and Technology*
of Organoelement Compounds, Shosse Entuziasov 38, 111 123 Moscow, U.S.S.R.

A systematic investigation of the recently described method for the synthesis of η6-arenetricarbonylchromium complexes has been performed. The method gives the fair to excellent yields of complexes in a broad range of benzene derivatives and of some benzenoid arenes. Very low yields of products were obtained with benzene, 2-(2-chlorophenyl)- and 2-(3-fluorophenyl)-1,3--dioxolane. The method failed in the case of benzaldehyde, benzoic acid, benzyl chloride, nitrobenzene, thiophenol and chalcone.

The new method for the synthesis of η6-arenetricarbonylchromium complexes has been described by us recently[1]. The method is based on utilization of a special adapter which allows to perform the complexation in boiling decalin, to shorten considerably the reaction time as well as to improve yields of the complexes. The method gives comparable or better yields than the most used Pauson and Mahaffy method[2], namely in the case of naphthalene, toluene, N,N-dimethylaniline, esters of benzoic and phenylacetic acids, but much lower yields in the case of chloro- and fluorobenzene.

The main aim of this work was to explore this method for complexation of different arenes and benzene derivatives.

All experiments described in this paper were carried out according to the general procedure given in the Experimental. The reaction was stopped when the evolution of CO ceased or when the decomposition of the product started. This was manifested by the colour change of the reaction medium from yellow or red to green.

As can be seen from Table I, the fair yields of the products were isolated at the complexation of phenanthrene and acenaphthene and the reaction time was short. The complexation of anthracene and acenaphthylene was going smoothly without decomposition of the product. Unfortunately we did not succeed in the isolation of the complexes because all the components (e.g. arene, Cr(CO)$_6$ and the complex) sublime very easily.

As already mentioned, our method[1] gives high yields of the chromium carbonyl complexes of some benzene derivatives. In this work we extended the series of benzene derivatives. The complexation of benzene itself gave poor results (3·5%). Pausion and Mahaffy method[2] gives 89% yield but after 40 h reaction time. The complexation of benzene using α-picoline as the catalyst[3] gives 95% yield but the reaction time is 4 − 5 days. The best method described up to now is the complexation in an autoclave in the presence of catalytic amount of pyridine[4] (93%, reaction time 8 h). The CO evolved should be released from the autoclave at the pressure of 0·7 to 0·8 MPa.

Tricarbonylchromium complexes of acetophenones and benzaldehydes are usually prepared via the complexation of their acetals or dioxolanes (see refs[5,6]) but yields are usually low. As seen in Table I the complexation of 2-phenyl- and 2-(2-fluorophenyl)-1,3-dioxolane went smoothly. Much lower yields of the products were isolated at the complexation of 2-(3-fluoro-, 4-fluoro- and 2-chlorophenyl)-1,3-dioxolanes. While we can anticipate that the low yields at the complexation of 2-chloro derivative can be caused by the well known reductive dechlorination observed at the complexation of chlorobenzene, we have no acceptable explanation for the low yields in the other two cases. Because of the easy complexation of benzophenone[1] we decided to attempt at complexation of acetophenone, benzaldehyde and benzoic

TABLE I

Results of the complexation of different arenes with $Cr(CO)_6$

No.	Arene complex	M.p., °C	Time h	Yield, %	
				this work	rep. (ref.)
1	Benzene	168−169	4	3·5	89(2)
2	Phenanthrene	156·5	4	85	27(10)
3	Acenaphthene	138−144	5	84	—
4	Anisole	84−85	6·5	70·7	85(2)
5	Phenol	113−115	14	41	23(11)
6	Thioanisole	104·5−106·5	2·5	85	—
7	Aniline	263 (dec)	2	80	44(11)
8	Acetophenone	83−85	1·5	48	35(12)
9	Stilbene	135−136	3	78	—
10	2-Phenyl-1,3-dioxolane	78−81	1	94	—
11	2-(2-Fluorophenyl)-1,3-dioxolane	104·5−106	4·5	56	14(13)
12	2-(3-Fluorophenyl)-1,3-dioxolane	93−95	5	17·5	—
13	2-(4-Fluorophenyl)-1,3-dioxolane	87−90	1·3	31	—
14	2-(2-Chlorophenyl)-1,3-dioxolane	110−114	0·75	13·7	11(13)

acid. The reasonable yield (34%) of the complex was isolated with acetophenone but in the other two cases and in the case of nitrobenzene the method failed, in accord with earlier observation[7,8].

To complete the range of benzene derivatives we performed the complexation of aniline, phenol, thiophenol, anisole and thioanisole. From the results given in the Table it is clear that all the experiments except of thiophenol gave desired yields. The complexation of thioanisole went 3 times more rapidly than the complexation of anisole. The complexation of phenol was much slower. Nevertheles, the crystalline complex, which decomposed on standing at room temperature overnight, was isolated. The complexation of thiophenol was unsuccessful; the reaction mixture turned black after several minutes of reflux.

It is well known that $Cr(CO)_3$ moiety enhances the reactivity of halogens bonded to the α- and β-carbon atom of alkylbenzenes. We decided, therefore, to perform the complexation of benzyl chloride. Instead of the yellow complex, a flocculate white precipitate was formed, being likely 1,2-diphenylethane, as described earlier[9].

As we are interested in the reactivity studies of chalcone complexes[6], we made also attempts at the chalcone complexation but in this case no complex has been isolated. This is rather surprising as the complexation of benzophenone, acetophenone or stilbene provided very well.

EXPERIMENTAL

All the solvents used in this work were carefully purified and dried. Special attention was paid to the purification of decalin. First it was distilled from sodium, then stirred with 10 vol. % of conc. H_2SO_4 at 100°C for 10 h. After separation it was refluxed for 8 h over sodium and then distilled under N_2 atmosphere. The solid arenes were purified either by sublimation (naphthalene, phenanthrene) or by crystallization (benzophenone). The liquid arenes were purified by distillation, and $Cr(CO)_6$, was sublimed prior to the use. The ¹H NMR spectra were measured at 80 MHz Tesla ES 587 instrument.

General Procedure for Complexation

The reaction mixture which consists of the arene and $Cr(CO)_6$ in the molar ratio 3·5 : 1 in decalin (100 ml of decalin for 0·01 mol of $Cr(CO)_6$) was purged for 20 min with argon, then it was evacuated for 20 min, and again argon was passed through it. This procedure was repeated 2—3 times. The reaction mixture was then refluxed until the evolution of CO ceased or decomposition of the complex started.

The reaction mixture was cooled to 20°C, and then to −18°C under argon. The crude product was filtered off, then dissolved in benzene and filtered through Kieselguhr. After concentration some light petroleum was added and the solution was left to crystallize at −18°C. From the residue which was insoluble in benzene some $Cr(CO)_6$ was recovered by sublimation at 80°C/10 Torr. The remainder of the product was isolated by chromatography of the decalin solution on a SiO_2 column. Decalin was eluted with petroleum ether, and the starting arenes were eluted either with petroleum ether/benzene 3 : 1 (naphthalene, phenanthrene) or petroleum ether/ethyl acetate 9·5 : 0·5 (v/v) (N,N-dimethylaniline, benzophenone). The complexes were eluted with

benzene/ethyl acetate 9·5 : 0·5 (v/v). All the products were crystalized from benzene/petroleum ether, they had correct elemental analyses and ^{1}H NMR spectra. The yields given in Table I are calculated on $Cr(CO)_6$ taken into the reaction.

New Compounds

(η^6-*Acenaphthene*)*tricarbonylchromium*). For $C_{15}H_{10}CrO_3$ (290·24) calculated: 62·07% C, 3·47% H; found: 62·66% C, 3·35% H. ^{1}H NMR ($C^2H_3COC^2H_3$): 3·82 m, 4 H (CH_2); 5·50 bs, 1 H, (Ar-Cr); 5·80 bs, 1 H (Ar-Cr); 6·25 bs, 1 H (Ar-Cr); 7·32 bs, 1 H (Ar); 7·50 bs, 2 H (Ar).

(η^6-*Stilbene*)*tricarbonylchromium*. For $C_{17}H_{10}CrO_3$ (314·27) calculated: 53·11% C, 2·67% H; found: 53·27% C, 2·59% H. ^{1}H NMR ($C^2H_3COC^2H_3$): 5·63—5·91 m, 5 H (C_6H_5—Cr); 6·9 d, 1 H (H_α, J_{AB} = 15); 7·30 d, 1 H (H_β, J_{AB} = 15); 7·35—7·70 m, 5 H (Ar).

(η^6-*Thioanisole*)*tricarbonylchromium*. For $C_{10}H_8CrO_3S$ (260·23) calculated: 46·15% C, 3·09% H; found: 46·04% C, 3·04% H. ^{1}H NMR ($C^2H_3COC^2H_3$): 2·50 s, 3 H (CH_3); 5·53 to 5·74 m, 5 H (C_6H_5).

(η^6-2-*Phenyl*-1,3-*dioxolane*)*tricarbonylchromium*. For $C_9H_{10}CrO_5$ (250·18) calculated: 50·34% C, 3·52% H; found: 50·41% C, 3·43% H. ^{1}H NMR ($C^2H_3COC^2H_3$): 4·07 m, 4 H (CH_2); 5·52—5·71 m, 6 H (C_6H_5 + $>$CH).

[η^6-2-(2-*Fluorophenyl*)-1,3-*dioxolane*]*tricarbonylchromium*. For $C_9H_9CrFO_5$ (304·20) calculated: 47·38% C, 2·98% H; found: 47·69% C, 2·93% H. ^{1}H NMR ($C^2H_3COC^2H_3$): 4·09 m, 4 H (CH_2); 4·87—5·62 m, 4 H (C_6H_4); 5·20 app.t, 1 H ($>$CH).

[η^6-2-(3-*Fluorophenyl*)-1,3-*dioxolane*]*tricarbonylchromium*. For $C_9H_9CrFO_5$ (304·20) calculated: 47·38% C, 2·98% H; found: 47·11% C, 2·48% H. ^{1}H NMR ($C^2H_3COC^2H_3$): 2·17 m, 4 H (CH_2); 5·25—5·82 m, 5 H (C_6H_5 + $>$CH).

[η^6-2-(4-*Fluorophenyl*)-1,3-*dioxolane*]*tricarbonylchromium*. For $C_9H_9CrFO_5$ (304·20) calculated: 47·38% C, 2·98% H; found: 47·91% C, 3·12% H. ^{1}H NMR ($C^2H_3COC^2H_3$): 4·06 d, 4 H (CH_2, J_{AB} = 4); 5·46 s, 1 H ($>$CH); 5·75 m, 3 H (C_6H_5, $H_{o,p}$); 6·00 m, 2 H (C_6H_5, H_m).

[η^6-2-(2-*Chlorophenyl*)-1,3-*dioxolane*]*tricarbonylchromium*. For $C_9H_9ClCrO_5$ (320·65) calculated: 44·95% C, 2·82% H; found: 45·12% C, 2·74% H. ^{1}H NMR ($C^2H_3COC^2H_3$): 4·05 m, 4 H (CH_2); 5·50—6·07 m, 4 H (C_6H_4); 5·37 app. t, 1 H ($>$CH).

REFERENCES

1. Hudeček M., Toma Š.: J. Organomet. Chem. *393*, 115 (1990).
2. Mahaffy C. A. L., Pauson P. L.: Inorg. Synth. *19*, 154 (1979).
3. Rausch M. D.: J. Org. Chem. *39*, 1787 (1974).
4. Magomedov G. K. I., Frenkel A. S., Blochina E. I.: Zh. Obshch. Khim. *55*, 1323 (1985).
5. Federič J., Toma Š., Gautheron B.: J. Organomet. Chem. *338*, 211 (1988).
6. Gajda V., Toma S., Widhalm M.: Monatsh. Chem. *120*, 147 (1989).
7. Willkinson G., Stone F. C. A., Abel E. W. (Eds): *Comprehensive Organometallic Chemistry*, Vol. 3, p. 1001. Pergamon Press, Oxford 1982.
8. Wender I., Pino I. (Eds): *Organic Synthesis via Metal Carbonyls*. Intersc. Publ., New York 1968.

9. Wey H. G., Butenschon M.: Chem. Ber. *123*, 93 (1990).
10. King R. B., Stone F. G. A.: J. Am. Chem. Soc. *82*, 4557 (1990).
11. Fischer E. O., Ofele K., Essler H., Frohlich W., Mortenson P., Semmlinger W.: Chem Ber. *91*, 2763 (1958).
12. Nicholls B., Whiting M. C.: J. Chem. Soc. *1959*, 551.
13. Ruppeldt J.: *Thesis*. Comenius University, Bratislava 1985.

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