SYNTHESIS OF ω-MERCURI- AND AND ω-LITHIOALKYLBENZENECHROMIUMTRICARBONYLS

V. S. Kaganovich and M. I. Rybinskaya

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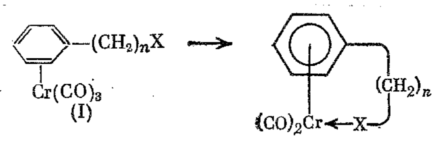
Organic mercury and lithium compounds have found extensive applications in synthetic organic and organometallic chemistry. Nevertheless, the synthesis of compounds of this type containing moieties bonded in the form of π-complexes have received little attention. We here report a study of the preparation of ω-mercuri- and ω-lithioalkylbenzenechromiumtricarbonyls.

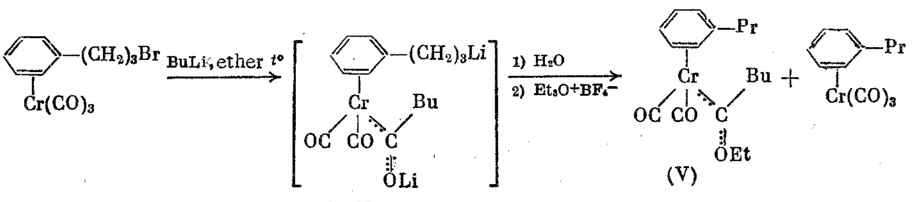
We have previously examined synthetic routes to arenechromiumtricarbonyl complexes (I) with ω-functional substituents in the alkyl side chain. In many instances, these complexes are readily converted into the chelates (II), in which the coordinating groups X are $CH=CH_2$, COR, COOEt, CN, and metal-containing groups [1-3]. It might be expected that attempts in this case to obtain (I) in which the group X contains mercury or lithium would instead afford chelates. It is known from the literature that mercuric chloride [4-6] and organomercury compounds (OMC) [7] form adducts with metal carbonyl complexes. Specifically, mercuric chloride gives a complex with benzenechromium tricarbonyl in which the mercury atom is coordinated simultaneously with the chromium atom and with the carbon of the carbonyl ligand [4]. Organolithium compounds are also known to react with the carbonyl groups of arenechromium tricarbonyls to form carbenes [8].



(I)

(II)

The starting materials used in this investigation were the ω-halo-substituted complexes $(CO)_3Cr \cdot Ph(CH_2)_nX$ (Ia-d), in which n=2, X=Cl (a), n=2, X=Br (b), n=3, X=Br (c), and n=4, X=Br (d). Complexes (Ia) and (Ib) have been described previously [9], but (Ic) and (Id) have been prepared for the first time by the same method. The preparation of ω-lithioalkylbenzenechromium tricarbonyls was first attempted by the reaction of complex (I) with BuLi, but it was found that the reaction of (Ib) and (Ic) with an excess of BuLi at −78°C (followed by treatment with water) gave only a small amount of the alkylbenzenechromium tricarbonyl, most of the starting material being recovered unchanged. However, when for example (Ic) was heated with BuLi in ether, compounds of type (III) were the main products (identified following treatment with water as propylbenzenechromium tricarbonyl), but in addition the highly unstable carbene complex (V) was isolated following treatment with $Et_3O^+BF_4^-$ [8]), identified by its mass spectrum [it is apparently formed via (IV)]. Thus, reaction of (I) with BuLi occurs primarily at the halogen atom, and to a lesser extent at the CO group



(IV)

(V)

We attempted to obtain the organolithium compound (III) by reacting (Ia-d) with metallic lithium. It was found that the complex (Ia) fails to react with lithium, even on boiling in ether, but (Ib-d) under these conditions afford small amounts of the organolithium compounds. Following treatment with water, the reaction mixture, in addition to decomposition products, always contained (from the mass spectra) a mixture of the starting material and the corresponding alkylbenzenechromium tricarbonyl. However, no traces of the carbene complex were found even after boiling in ether (as described in [8]). It is interesting that even after prolonged boiling of (Ic)

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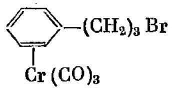
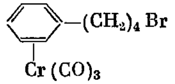
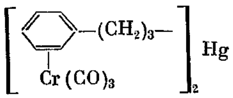
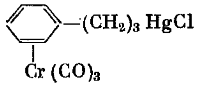
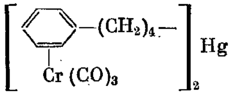
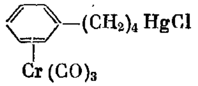
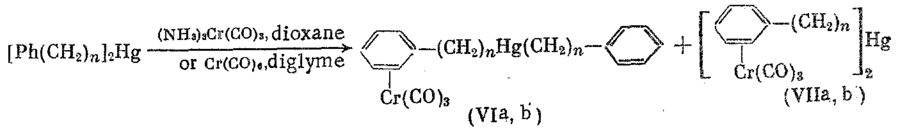
TABLE 1

Compound	Yield, %	mp, °C	Found, %			Empirical formula	Calculated, %			$\nu_{C\equiv O}$, cm^{-1}
			C	H	Cr		C	H	Cr	
	27	54–55 (from pentane)	43,51	3,53	15,77	$C_{12}H_{11}BrCrO_3$	43,01	3,31	15,52	1915, 1980
	28	Oil	45,22	3,74	14,80	$C_{13}H_{13}BrCrO_3$	44,71	3,75	14,89	1914, 1981
	18	127–129 (from pentane)	40,15	3,27	15,00	$C_{24}H_{22}Cr_2HgO_6$	40,54	3,12	14,63	1912, 1978
	52	114–115 (from aq. methanol)	29,45	2,23	10,40	$C_{12}H_{11}ClCrHgO_3$	29,34	2,26	10,59	1915, 1980
	15	3–5 (from pentane)	42,57	3,72	14,43	$C_{26}H_{26}Cr_2HgO_6$	42,25	3,55	14,07	1912, 1980
	50	90–92 (from aq. methanol)	30,56	2,14	9,91	$C_{13}H_{13}ClCrHgO_3$	30,90	2,59	10,29	1913, 1980

with lithium in diisopropyl ether, small amounts of starting material remained. The reason for the slowness of the reaction is unclear.

We also attempted to synthesize (III) by reacting the appropriate OMC such as $Ph(CH_2)_nHgX \cdot Cr(CO)_3$ or $[Ph(CH_2)_n]_2Hg \cdot [Cr(CO)_3]_2$ with metallic lithium (as described in [10]). These OMC, which have a mercury atom in the ω-position of the side chain, are of independent interest, since the possibility of the intramolecular coordination of the mercury atom with Cr or the CO groups could not be excluded (such as is described for example in [4]). It is reported in the literature [11] that the direct reaction of for instance PhHgCl with $Cr(CO)_6$ gives only decomposition products. We attempted to obtain the chromium tricarbonyl derivative of $Ph(CH_2)_3HgBr$ under milder conditions, but the reaction of $Ph(CH_2)_3HgBr$ with $(NH_3)_3Cr(CO)_3$ in boiling dioxane likewise failed to give the desired product. However, when the reaction was carried out with $Py_3Cr(CO)_3$ in the presence of $BF_3 \cdot OEt_2$ at ~20°C, i.e., under the mildest conditions [9], only traces of the chromium tricarbonyl complexes were obtained. It is possible that the presence of OMC inhibits the reaction, since the salt could form complexes with the $Py_3Cr(CO)_3$. However, the symmetrical OMC $[Ph(CH_2)_n]_2Hg$ gives the chromium tricarbonyl complexes. These symmetrical products were obtained by treating $Ph(CH_2)_nHgBr$ with the appropriate Grignard reagent $Ph(CH_2)_nMgBr$. On reaction with $(NH_3)_3Cr(CO)_3$ or $Cr(CO)_6$, they afford a mixture of mono- and binuclear complexes (VI) and (VII). The products (VI) and (VII) were separated by preparative TLC on alumina.

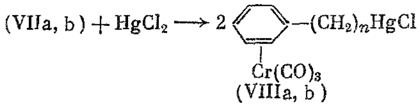


$n = 3$ (a), 4 (b)

It is interesting that in the reaction of $[Ph(CH_2)_n]_2Hg$ with even a large excess of $(NH_3)_3Cr(CO)_3$, a mixture of (VI) and (VII) was always obtained, whereas it has been reported [12] that under the same conditions dibenzylmercury gives only the binuclear derivative. Additional amounts of (VII) may be obtained by boiling (VI) with $(NH_3)_3Cr(CO)_3$ in dioxane.

The mercury atom in complexes (VI) and (VII) is apparently not coordinately bonded to the chromium atom or the CO groups, since in the $\nu C \equiv O$ region there is virtually no difference from the IR spectra of (Ic) and (Id), whereas it is known that when coordinated with the mercury atom the positions and numbers of the bands in the metal carbonyl region change markedly [4-6]. We then tried to use the complex (VII) to prepare the corresponding ω-lithioalkyl derivative by reaction with metallic lithium, but even after prolonged stirring in boiling ether the starting material was largely recovered unchanged, i.e., replacement of mercury by lithium, which normally takes place at temperatures as low as ~20°C [10], did not take place.

Treatment of the symmetrical complexes (VII) with mercuric chloride converted them into the nonsymmetrical OMC (VIII). The compounds (VIII) were solids which were stable indefinitely in air. Their IR spectra



$n = 3$ (a), 4 (b)

also indicate the absence of coordination of the mercury atom with the chromium atom or the CO groups. We are currently engaged in a detailed examination of the chemical properties of the ω-mercurated benzenechromium tricarbonyls obtained.

Thus the synthesis of ω-lithio- and mercurated derivatives of arenechromium tricarbonyl complexes such as $X(CH_2)_nC_6H_5 \cdot Cr(CO)_3$ (X = Li, HgCl) is attended by difficulties which are not attributable to intramolecular interactions of the ω-X groups with the chromium tricarbonyl group. These difficulties can be surmounted only in the synthesis of mercury complexes using the symmetrical compounds $[Ph(CH_2)_n]_2Hg$ by reaction with chromium carbonyls. The subsequent reactions of the compounds with mercuric chloride proceed without complications.

EXPERIMENTAL

Complexes (Ic) and (Id) were obtained by methods similar to that described in [9], and their yields and melting points are shown in Table 1. IR spectra were obtained in cyclohexane on an IKS-14A spectrophotometer.

Preparations of $Ph(CH_2)_3HgBr$. To the Grignard reagent obtained from 2.5 g of magnesium and 20.5 g of $Ph(CH_2)_3Br$ in 50 ml of dry ether was added 42 g of $HgBr_2$, and the mixture was boiled with stirring for 2 h. After cooling to ~20°C, the mixture was decomposed with water, the organic layer separated, washed with dilute hydrochloric acid and water (twice), and dried over calcium chloride. After removing the ether in vacuo, the residue was washed with pentane and recrystallized from methanol to give 25 g (61%) of a colorless solid, mp 49-50°C (from methanol). Found: C 27.00; H 2.87; Br 19.94; Hg 49.90%. $C_9H_{11}BrHg$. Calculated: C 27.04; H 2.77; Br 19.99; Hg 50.19%.

Preparation of $[Ph(CH_2)_3]_2Hg$. To the Grignard reagent obtained from 3.4 g of magnesium and 24.3 g of $Ph(CH_2)_3Br$ in 100 ml of dry ether was added a solution of 25 g of $Ph(CH_2)_3HgBr$ in 100 ml of dry ether. The mixture was boiled with stirring for 4 h, decomposed with water and ammonium chloride, the organic layer separated, and the aqueous layer extracted with ether (2 × 50 ml). After drying over Na_2SO_4, the solvent was removed in vacuo, and the residue distilled at 130-150°C ($8 \cdot 10^{-4}$ mm) to give 10.5 g (38%) of a colorless liquid which partially decomposed on distillation, rendering it impossible to obtain a satisfactory elemental analysis. The product was identified by its mass spectrum. $[Ph(CH_2)_4]_2Hg$ was obtained similarly.

Reaction of $[Ph(CH_2)_3]_2Hg$ with $(NH_3)_3Cr(CO)_3$. A mixture of 4.4 g (0.01 mole) of $[Ph(CH_2)_3]_2Hg$ and 4 g (0.021 mole) of $(NH_3)_3Cr(CO)_3$ in 50 ml of dioxane was boiled for 6 h under argon.

The solution was filtered, and the solvent removed in vacuo. The residue was separated by preparative TLC on alumina with a 2 : 1 mixture of benzene and heptane. The two yellow bands were collected, and from the first the complex (VIa) was obtained as a yellow oil (39%), identified by its mass spectrum ($[M]^+ = 572-576$, corresponding to the isotope distribution of mercury (198-202); from the second band there was obtained complex (VIIa) as a yellow solid (yield and elemental analysis shown in Table 1). The IR spectra of the two compounds were identical in the $\nu C \equiv O$ region. These compounds can also be obtained, but in smaller yields, by boiling $[Ph(CH_2)_3]Hg$ with $Cr(CO)_6$ in diglyme.

Reaction of $[Ph(CH_2)_4]_2Hg$ with $(NH_3)_3Cr(CO)_3$. Obtained similarly were (VIb), yield 25%, yellow oil, identified by its mass spectrum ($[M]^+ = 601-605$), $\nu C \equiv O$ 1913, 1981 cm^{-1}, and (VIIb) (see Table 1).

Reaction of (VIIa) with Lithium. A solution of 0.71 g (1 mmole) of (VIIIa) in 50 ml of dry ether and 0.1 g of finely divided lithium was stirred under argon at ~20°C for 1 h, then boiled for 5 h, during which time the yellow color of the solution remained unchanged. The solvent was removed in vacuo, and the residue separated by preparative TLC on alumina. In addition to decomposition products, two yellow bands were present. The first afforded 0.06 g of (VIa) (from its mass spectrum), and the second gave 0.41 g (58%) of the starting material (VIIa) (identified by its R_f value, IR spectrum, and melting point).

Preparation of $Ph(CH_2)_nHgCl \cdot Cr(CO)_3$. A mixture of 1 mmole of (VII) and 1 g (3.5 mmole) of $HgCl_2$ in 100 ml of n-butanol sealed in an ampul under argon was heated at 80-85°C for 8 h with periodic shaking. The solution was filtered hot, evaporated to ~1/4 of its original volume, and cooled. The yellow crystals of (VIII) which separated were filtered off, washed with pentane, dried, and recrystallized from aqueous methanol. The properties of the products are shown in Table 1.

CONCLUSIONS

1. Reaction of $[Ph(CH_2)_n]_2Hg$ ($n = 3, 4$) with $(NH_3)_3Cr(CO)_3$ or $Cr(CO)_6$ affords the corresponding mono- and binuclear arenechromium tricarbonyl derivatives.

2. Treatment of the complexes $[Ph(CH_2)_n]_2Hg \cdot [Cr(CO)_3]_2$ with mercuric chloride gives the ω-chloromercuri-substituted arenechromium tricarbonyls $(CO)_3Cr \cdot Ph(CH_2)_nHgCl$ ($n = 3, 4$), in which the mercury atom is not coordinated with the $Cr(CO)_6$ groups.

3. The formation of ω-lithioalkylbenzenechromium tricarbonyls from the ω-bromo compounds $(CO)_3Cr \cdot Ph(CH_2)_nBr$ ($n = 2, 4$) by standard methods proceeds with difficulty, and is accompanied by a number of byproducts.

LITERATURE CITED

1. A. N. Nesmeyanov, M. I. Rybinskaya, V. V. Krivykh, and V. S. Kaganovich, J. Organomet. Chem., 93, C8 (1975).
2. A. N. Nesmeyanov, V. S. Kaganovich, V. V. Krivykh, and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 156 (1977).
3. A. N. Nesmeyanov, M. I. Rybinskaya, V. S. Kaganovich, and L. M. Korneva, Izv. Akad. Nauk SSSR, Ser. Khim., 722 (1978).
4. G. K.-I. Magomedov, A. I. Gusev, A. S. Frenkel', V. G. Syrkin, L. I. Chaplina, and S. N. Gurkova, Koordinats. Khim., 2, 257 (1976).

5. K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, J. Chem. Soc., A 2851 (1968).
6. B. V. Lokshin, A. G. Ginzburg, and E. B. Nazarova, Usp. Khim., 49, 223 (1980).
7. F. Glockling, V. B. Mahale, and J. J. Sweeney, J. Chem. Soc. Dalton Trans., 767 (1979).
8. E. O. Fischer, P. Stucker, H.-J. Beck, and F. R. Kreissl, Chem. Ber., 109, 3089 (1976).
9. A. N. Nesmeyanov, M. I. Rybinskaya, and V. S. Kaganovich, Izv. Akad. Nauk SSSR, Ser. Khim., 2824 (1978).
10. T. V. Talalaeva and K. A. Kecheshkov, Methods of Heteroorganic Chemistry. Li, Na, K, Rb, and Cs [in Russian], Moscow (1971), Vol. 1, p. 468.
11. M. D. Rausch and R. E. Gloth, J. Organomet., Chem., 153, 59 (1978).
12. G. A. Razuvaev, A. N. Artemov, T. G. Kasatkina, and E. N. Poselenova, Izv. Akad. Nauk SSSR, Ser. Khim., 1131 (1982).

FACTORS DETERMINING TRANSFORMATIONS OF SILICON-CONTAINING AROXYLS.

COMMUNICATION 1. DISPROPORTIONATION AND DIMERIZATION-REARRANGEMENT AS ALTERNATIVE TRANSFORMATION PATHS OF SILICON-CONTAINING AROXYLS

D. V. Muslin and N. Sh. Lyapina

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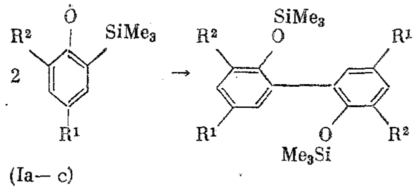
It is known [1] that replacement of at least one ortho-tert-butyl group of the stable 2,4,6-tri-tert-butylphenoxyl radical by the trimethylsilyl group leads to the appearance of a new type of transformation, namely, dimerization-rearrangement of silicon-containing aroxyls. The reaction products are tetrasubstituted 2,2'-bis(trimethylsilyloxy)diphenyls

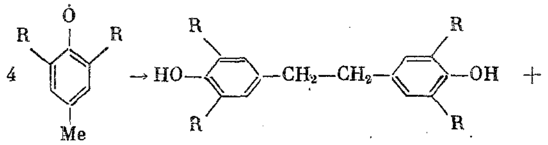


(Ia– c)

$R^1 = R^2 = t$-Bu (Ia); $R^1 = t$-Bu, $R^2 = Me_3Si$ (Ib); $R^1 = R^2 = Me_3Si$ (Ic).

The stability of aroxyls obtained by oxidizing 2,6-di-tert-butyl-4-alkylphenols depends on the type of the para-alkyl substituent [2]. In the presence of para-alkyl groups with α-hydrogen atoms, the phenoxyl radicals disproportionate to form methylenequinone and the initial phenol. The rate of disproportionation decreases in the following series of para-alkyl substituents: Me > Et > $CHMe_2$ > cyclo-C_6H_{11}.

For 2,6-bis(trimethylsilyl)-4-alkylphenoxyls, both disproportionation and dimerization-rearrangement are, in principle, possible, and the character of the transformation of the aroxyl radical depends on the para-alkyl substituent. Thus, 2,6-bis(trimethylsilyl)-4-methylphenoxyl (II) disproportionates to form products of the same type as in the case of its carbon analog (R = t-Bu).



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