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Transition Metal Carbene Complexes, LXa. 1,1-Dihalo-2-phenylvinyl Methyl Ethers from [Phenyl(methoxy)carbene]pentacarbonylchromium(0) and Phenyl(trihalomethyl)mercurials[1]

A. DE RENZI and E. O. FISCHER
Inorganic Chemical Laboratory, Technical University Munich, D8 Munich 2, Arcisstr. 21, Germany
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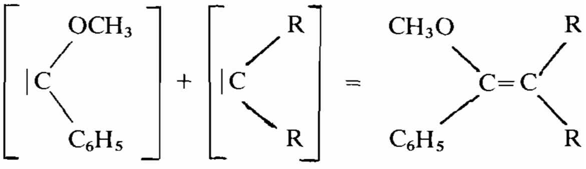
[Phenyl(methoxy)carbene]pentacarbonylchromium(0) reacts with phenyl(trihalomethyl)mercury compounds (Hal = Cl, Br) to give the 1,1-dihalo-2-phenylvinyl methyl ethers. Among the organic reactions products, benzophenone was isolated in significant amounts. This compound was proved to be formed by reaction between the chromium–carbene complex and the phenylmercuric halides derived by decomposition of the starting mercurials.

Introduction

The chemistry of the transition metal–carbene complexes has undergone, in the last years, an enormous development.[2] Actually, stable metal–carbene complexes are of great interest as possible reagents for organic syntheses involving the transfer of the carbene ligand. In particular, [phenyl(methoxy)carbene]pentacarbonyl complexes of chromium(0), molybdenum(0) and tungsten(0) are known to react with olefins[3–5] yielding cyclopropane derivatives and with $(C_6H_5)_2SiH_2$ [6] giving insertion of the carbene moiety into the Si–H bond.

On the other hand, heating [phenyl(methoxy)carbene] pentacarbonylchromium(0) in the absence of such reactive substrates results[7] in the formation of a mixture of *cis* and *trans*-α,α'-dimethoxystilbene, by dimerization of the carbene residue.

In order to obtain further data about the reactivity of these complexes, it seemed to be interesting to carry out the decomposition of $(CO)_5CrC(OCH_3)C_6H_5$ in the presence of another carbene precursor. As the "free" carbene ligand $C(OCH_3)C_6H_5$ should preferably display nucleophilic properties, it should be possible, in principle, that the presence in the reaction system of an electrophilic carbene source, could give rise to an olefinic compound formed by interaction of these two different carbene residues (eq. 1):



(1)

R = Electron-withdrawing substituents

As source of an electrophilic carbene we have chosen organomercury compounds of the type $C_6H_5HgCX_3$ (X = halogen) that have been found to be very effective dihalocarbene precursors.[8] These compounds seemed to be particularly attractive in our investigations owing to the possibility, by varying X and/or the organic group bonded to mercury, to have dihalocarbene sources with a wide range of reactivity.

In this paper we report the results obtained in the reactions between $(CO)_5CrC(OCH_3)C_6H_5$ and $C_6H_5HgCX_3$ compounds (X = Cl, Br). Also *cyclo*-$C_6H_{11}HgCCl_2Br$[9] was used, but no reaction was observed under our experimental conditions.

Experimental Section

All reactions were carried out in prepurified nitrogen. Solvents were dried over sodium and stored and handled under nitrogen. G.l.c. analyses were performed on a Perkin–Elmer Mod. 116 gas chromatograph using columns packed with SE 52 on Chromosorb G or Apiezon M on Celite 545. For preparative purposes a Hupe APG 402 gas-chromatograph was used with a 2 m × 20 mm o.d. column of 20% SE 30 on Chromosorb P. Mass spectra were recorded on an Atlas CH4.

[Phenyl(methoxy)carbene]pentacarbonylchromium(0) was prepared using the known procedure.[7] $C_6H_5HgCCl_3$, $C_6H_5HgCCl_2Br$ and $C_6H_5HgCBr_3$ were prepared as described.[10] In the case of *cyclo*-$C_6H_{11}HgCCl_2Br$ a procedure as in ref. 10a was used instead of that recently[9] reported. A reaction time reduced to ten minutes and the work-up of the reaction mixture as soon as possible, gave satisfactory results. An authentic sample of 1,1-dichloro-2-phenylvinyl methyl ether was synthesized as reported in the literature.[11]

Reaction of $(CO)_5CrC(OCH_3)C_6H_5$ with $C_6H_5HgCCl_3$

6.24 g(0.02 mol) of $(CO)_5CrC(OCH_3)C_6H_5$ and 8.72 g(0.022 mol) of $C_6H_5HgCCl_3$ were dissolved in 30 ml of dry benzene under prepurified nitrogen. The mixture was stirred and heated at reflux for 24 h. During this period the red solution turned brown and a precipitate containing some metallic mercury was formed. After cooling to room temperature, the mixture was filtered and the solid residue was washed with 10 ml of benzene. The red-brown filtrate was carefully evaporated at 25°/20 mm to remove benzene. The residue was distilled trap-to-trap under high vacuum yielding about 1.2 g of a yellow oil. After a gaschromatographic analysis of this crude material, the 1,1-dichloro-2-phenylvinyl methyl ether, identified by comparison of its retention time with that of an authentic sample, was purified by preparative gas-chromatography using a 2 m × 20 mm o.d. column of 20% SE 30 on Chromosorb P operating at 200° with a nitrogen flow of 0.5 l/min. *Anal.* Calcd. $[C_9H_8Cl_2O]$: C, 53.25; H, 3.97; Cl, 34.92; O, 7.87. Found: C, 53.61; H, 3.98; Cl, 34.70; O, 7.50. The mass spectrum showed the molecular peak at *m/e* 202 (202.15 calculated on the basis of ^{35}Cl).

The ^1H-NMR spectrum, recorded in CCl_4 with TMS as internal standard, showed two resonance peaks at 2.54 τ (5H, C_6H_5) and 6.55 τ (3H, OCH_3).

The IR-spectrum recorded on pure liquid showed bands at 3030(w), 2976(w), 2915(m), 2817(w), 1613(w), 1592(m), 1570(w), 1488(m), 1441(m), 1285(s), 1267(s), 1185(m), 1104(vs), 1071(m), 1027(m), 1002(vs), 908(vs), 823(s), 766(vs), 738(w), 697(vs) cm^{-1}. In addition to the expected product, the crude material obtained in this reaction contained some amounts of methyl benzoate and benzophenone, the latter being significant. These products were identified by comparison with authentic samples.

Reaction of $(CO)_5CrC(OCH_3)C_6H_5$ with $C_6H_5HgCCl_2Br$

0.94 g (0.003 mol) of $(CO)_5CrC(OCH_3)C_6H_5$ and 1.54 g (0.0035 mol) of $C_6H_5HgCCl_2Br$ were dissolved in 10 ml of dry benzene and heated under stirring for 12 h at the boiling point. After cooling to room temperature, the mixture was filtered and the residue washed with 2 ml of benzene. The filtrate, after removal of the major part of the benzene, was distilled trap-to-trap. A gas-chromatographic analysis showed the presence of the 1,1-dichloro-2-phenylvinyl methyl ether in a yield somewhat lower than that obtained in the previous reaction.

Reaction of $(CO)_5CrC(OCH_3)C_6H_5$ with $C_6H_5HgCBr_3$

6.24 g (0.02 mol) of $(CO)_5CrC(OCH_3)C_6H_5$ and 11.65 g (0.022 mol) of $C_6H_5HgCBr_3$ were dissolved in 40 ml of dry benzene and heated, under stirring, for 12 h. After cooling to room temperature, the mixture was worked up as previously described. After distillation, the amount of the obtained material was found to be too low to attempt a separation. However a gas-chromatographic analysis showed the presence of two main products, that gave in the mass spectrum, molecular peaks at *m/e* 290 (1,1-dibromo-2-phenylvinyl methyl ether has a mol.wt. of 290.15 calculated on ^{79}Br) and at *m/e* 340 (tetrabromoethylene has a mol.wt. of 340.02 calculated on ^{79}Br).

Reaction of $(CO)_5CrC(OCH_3)C_6H_5$ and cyclo-$C_6H_{11}HgCCl_2Br$

0.94 g (0.003 mol) of $(CO)_5CrC(OCH_3)C_6H_5$ and 1.56 g (0.0035 mol) of $C_6H_{11}HgCCl_2Br$ were dissolved in 10 ml of dry benzene and stirred at room temperature for 3 days. After filtration of a small amount of precipitate, and removal of benzene, only a solid material was obtained. Extracting with *n*-pentane, a white solid was recovered, that was found to be a mixture of unreacted $C_6H_{11}HgCCl_2Br$ and $C_6H_{11}HgBr$. Evaporating the pentane solution unreacted chromium–carbene complex was obtained.

Reaction between $C_6H_5HgCCl_3$ and $C_6H_5COOCH_3$ in Presence of $(C_6H_5)_3P$

0.80 g (0.002 mol) of $C_6H_5HgCCl_3$, 0.14 g (0.002 mol) of methyl benzoate and 0.50 g (0.002 mol) of triphenylphosphine were dissolved in 10 ml of dry benzene and allowed to react for 24 h under stirring at the boiling point. After cooling to room temperature, the light yellow solution was filtered, and the major part of benzene was removed *in vacuo*. A g.l.c. analysis of the residue did not show the presence of 1,1-dichloro-2-phenylvinyl methyl ether. Only a small broad signal just above the zero-line was observed, the instrument being used at maximum of its sensitivity.

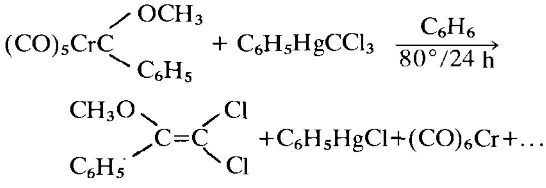
Reaction of $(CO)_5CrC(OCH_3)C_6H_5$ with C_6H_5HgBr

To 0.78 g (0.0025 mol) of $(CO)_5CrC(OCH_3)C_6H_5$ dissolved in 10 ml of dry benzene, 0.90 g (0.0025 mol) of C_6H_5HgBr was added. The red mixture was stirred under nitrogen and heated to the boiling point for 24 h. During this period mercury metal was observed to form. After cooling to room temperature, the light yellow solution was filtered and the solid residue washed with a little benzene. A g.l.c. analysis of the solution showed the presence of benzophenone, identified by comparison with an authentic sample. Also a little amount of methyl benzoate was found.

To achieve a full identification, the benzene solution was evaporated *in vacuo* and the oily residue, dissolved in a few drops of ethanol, was added to a warm solution of 0.5 g of 2,4-dinitrophenylhydrazine in 10 ml of 10:1 ethanol/concentrated hydrochloric acid. Heating briefly to the boiling point, a red crystalline solid began to precipitate. The solid was filtered, washed with ethanol and dried. 0.38 g of crude hydrazone were obtained. After recrystallizations from ethanol and benzene, this material had a melting point of 238°. A mixed melting point with an authentic sample was not depressed. *Anal.* Calcd. [$C_{19}H_{14}N_4O_4$]: C, 62.98; H, 3.89; N, 15.46. Found: C, 63.01; H, 3.66; N, 15.13.

Results and Discussion

When $(CO)_5CrC(OCH_3)C_6H_5$ and $C_6H_5HgCCl_3$ are heated at the boiling point in an inert solvent such as benzene for 24 h, 1,1-dichloro-2-phenylvinyl methyl ether is formed in about 20% yield. The formation of this compound can be simply explained in terms of an interaction between the dichlorocarbene CCl_2, released from the organomercurial by thermal decomposition, and the carbene ligand bonded to chromium(0). A schematic, non stoichiometric equation can be used to represent this process (eq. 2):

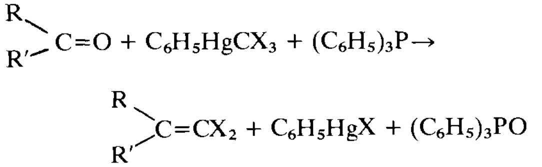


$$(CO)_5CrC(OCH_3)(C_6H_5) + C_6H_5HgCCl_3 \xrightarrow[80°/24\,h]{C_6H_6} (CH_3O)(C_6H_5)C{=}CCl_2 + C_6H_5HgCl + (CO)_6Cr + \ldots \quad (2)$$

It must be noted that, in reactions involving organometallic compounds, the main reaction products are usually always accompanied by other by-products. This fact was found particularly true in our case, in that a quite complete decomposition of the reactants was not related to a corresponding high yield of the expected products. Indeed, the solid reaction residue contained, in addition to the expected C_6H_5HgCl, $(CO)_6Cr$ and other unidentified chromium compounds a significant amount of mercury metal. On the other hand, the gas-chromatographic analysis of the filtered benzene solution showed the presence of other products, different from 1,1-dichloro-2-phenylvinyl methyl ether and tetrachloroethylene, that could be formed[8] by dimerization of the dichlorocarbene. Two of these organic compounds were identified as methyl benzoate and benzophenone, the last being present in amount comparable to that of the substituted vinyl methyl ether.

The organomercurials $C_6H_5HgCCl_2Br$ and $C_6H_5HgCBr_3$ gave similar results. On the contrary, using the more reactive[9] *cyclo*-$C_6H_{11}HgCCl_2Br$ no reaction was obtained and the chromium–carbene complex was recovered unchanged. These experimental data are summarized in Table I.

The presence of methyl benzoate and benzophenone, among the reaction products, requires explanation. The simplest explanation for the formation of methyl benzoate is that it is due to an oxidation of the chromium-carbene complex by traces of oxygen in the reaction system. However, regardless of the mechanism of its formation, the following question arises. It is known[12] that phenyl(trihalomethyl)mercurials can react with ketones or aldehydes in presence of triphenylphosphine giving substituted ethylenes (eq. 3):



$$RR'C{=}O + C_6H_5HgCX_3 + (C_6H_5)_3P \rightarrow RR'C{=}CX_2 + C_6H_5HgX + (C_6H_5)_3PO \quad (3)$$

Triphenylphosphine is likely to be involved in the formation of an ylide intermediate and acts as oxygen-acceptor. It could be possible, in our case, that a reaction in which the mercurial reacts directly with the benzoic ester (eq. 4 and 4′) takes place.

TABLE I. Reactions of $(CO)_5CrC(OCH_3)C_6H_5$ with $RHgCX_3$.

$RHgCX_3$ (decomp. way)	Reaction Conditions[a]	Organic Products
$C_6H_5HgCCl_3$ ($C_6H_5HgCl+CCl_2$)	24h/80°	$C_6H_5C(OCH_3){=}CCl_2$, $(C_6H_5)_2CO$, $C_6H_5COOCH_3$, ($CCl_2{=}CCl_2$)
$C_6H_5HgCCl_2Br$ ($C_6H_5HgBr+CCl_2$)	12h/80°	$C_6H_5C(OCH_3){=}CCl_2$, $(C_6H_5)_2CO$, $C_6H_5COOCH_3$, ($CCl_2{=}CCl_2$)
$C_6H_5HgCBr_3$ ($C_6H_5HgBr+CBr_2$)	12h/80°	$C_6H_5C(OCH_3){=}CBr$, $(C_6H_5)_2CO$, $C_6H_5COOCH_3$, $CBr_2{=}CBr_2$
$C_6H_{11}HgCCl_2Br$ ($C_6H_{11}HgBr+CCl_2$)	3 days/20°	–

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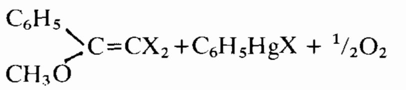
[a] Reactions were carried out in dry benzene, with stirring under nitrogen.

$$(CO)_5CrC(OCH_3)C_6H_5 + O_2 \rightarrow C_6H_5COOCH_3 + \ldots \quad (4)$$

$$C_6H_5COOCH_3 + C_6H_5HgCX_3 \rightarrow$$



$$(C_6H_5)(CH_3O)C{=}CX_2 + C_6H_5HgX + {}^1/_2O_2 \quad (4')$$

The oxygen released in this process oxidizes another molecule of the chromium–carbene complex, thus reforming the benzoic ester. Although this hypothesis cannot be completely ruled out, it seems to us unreliable and, however, it must be noted that no identifiable amount of this substituted ethylene was found when $C_6H_5HgCCl_3$ was allowed to react with $C_6H_5COOCH_3$ in presence of triphenylphosphine.

With regard to the presence of benzophenone in a relatively high amount in the crude reaction mixture, it seemed necessary to obtain more experimental information. Indeed, we have found that benzophenone is formed in high yield when $(CO)_5CrC(OCH_3)C_6H_5$ reacts with phenylmercuric halide. This reaction is accompanied by a reduction of Hg^{II} to Hg^0 (eq. 5):

$$(CO)_5CrC(OCH_3)C_6H_5 + C_6H_5HgX \rightarrow (C_6H_5)_2CO + Hg + \ldots \quad (5)$$

As phenylmercuric halide is formed during the thermal decomposition of phenyl(trihalomethyl)mercurials, the finding of benzophenone and mercury metal in our previously described reactions is fully understood. The reaction schematically reported in eq. 5 is surprising and, at this moment, no suitable mechanism can be proposed. More experimental work has to be undertaken to elucidate this process. We can only mention that phenylmercuric halides are known[13] to react under very mild conditions with CO in presence of Pd^{II} or Rh^{III} compounds to give in fair yields benzophenone (eq. 6):

$$2\,C_6H_5HgCl + CO + PdCl_2 \rightarrow (C_6H_5)_2CO + 2\,HgCl_2 + Pd \quad (6)$$

The mechanism of this process is not quite clear, but it is supposed that the first step is the formation of a phenyl–palladium (or rhodium) derivative, followed by a CO insertion. Reaction of this acyl intermediate with the starting mercuric compound or with the previously formed phenyl–palladium (or rhodium) gives rise to benzophenone. It should be noted that, if methanol is used as solvent, the formation of methylbenzoate also occurs. It could be possible that also in our case a similar mechanism is to be claimed, as a chromium carbonyl complex is involved. However, at the present no clear evidences can be given. As a last point, it can be noted, observing the experimental results, that the yields of 1,1-dihalo-2-phenylvinyl methyl ether are reversed with regard to the reactivity of the mercurials. Using the cyclohexyl derivative, that is reported[9] to transfer CCl_2 to a carbenophile in 2 days at room temperature and in few minutes at 80°, no reaction was obtained at room temperature after 3 days. On the contrary, the best result was achieved using $C_6H_5HgCCl_3$, that has, even at 80°, a relatively slow CCl_2 transfer rate. This fact is obviously related to the mechanism of this reaction. It is not yet clear if reactions in which a carbene moiety is transferred from a metal–carbene complex to an organic substrate proceed *via* an interaction of these two reactants, or only the "free" carbene is involved. Recent investigations support the former hypothesis. Indeed, it was shown[4] that, in the reactions of [phenyl(methoxy)carbene]pentacarbonyl complexes of chromium(0), molybdenum(0) and tungsten(0) with *trans*-methyl crotonate or diethyl maleate, the ratio of the two obtained isomeric cyclo-propane derivatives depends strongly on the metal. In addition, reaction of (*R*)-methylphenylpropylphosphine[phenyl(methoxy)carbene]tetracarbonylchromium(0) with diethyl fumarate yielded[14] an optically active cyclo-propane derivative, thus proving the existence of an interaction of the olefin with the metal complex. In our case, the observation that the best results are obtained using a mercurial that decomposes at almost the same rate as the chromium–carbene complex, seems to suggest that this reaction may involve "free" carbenes. However, these experimental features are not enough to allow reasonable hypotheses on the mechanism. In addition, our system shows a complexity owing to an important side reaction, whose mechanism is also to be clarified. Therefore, other experimental data, using a variety of metal–carbene complexes, appear to be necessary before this problem can be settled.

Acknowledgements

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References

1 For Part LX of this series see E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem., 85,* 618 (1973).

2 D.J. Cardin, B. Cetinkaya, and M.F. Lappert, *Chem. Rev., 72,* 545 (1972).

3 E.O. Fischer and K.H. Dötz, *Chem. Ber., 103,* 1273 (1970).

4 K.H. Dötz and E.O. Fischer, *Chem. Ber., 105,* 1356 (1972).

5 E.O. Fischer and K.H. Dötz, *Chem. Ber., 105,* 3966 (1972).

6 E.O. Fischer and K.H. Dötz, *J. Organometal. Chem., 36,* C4 (1972).

7 E.O. Fischer, B. Heckl, K.H. Dötz, J. Müller, and H. Werner, *J. Organometal. Chem., 16,* P29 (1969).

8 D. Seyferth, J.M. Burlitch, R.J. Minasz, J. Yick–Pui Mui, H.D. Simmons, Jr., A.J.H. Treiber, and S.R. Dowd, *J. Am. Chem. Soc., 87,* 4259 (1965).

9 D. Seyferth and C.K. Haas, *J. Organometal. Chem., 46,* C33 (1972).
10a D. Seyferth and J.M. Burlitch, *J. Organometal. Chem., 4,* 127 (1965).
10b D. Seyferth and R.L. Lambert, Jr., *ibid., 16,* 21 (1969).
11 W. Ruske and I. Hartmann, *J. Prakt. Chem., 18,* 146 (1962).
12 D. Seyferth, J.K. Heeren, G. Singh, S.O. Grim, and W.B. Hughes, *J. Organometal. Chem., 5,* 267 (1966).
13 R.F. Heck, *J. Am. Chem., Soc., 90,* 5546 (1968).
14 M.D. Cooke and E.O. Fischer, *J. Organometal. Chem., 56,* 279 (1973).