Journal of Organometallic Chemistry, 166 (1979) 217—222
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

NEW METHODS OF SYNTHESIS OF σ-ETHYNYLMETAL CARBONYL DERIVATIVES

A.N. NESMEYANOV *, L.G. MAKAROVA, V.N. VINOGRADOVA, V.N. KORNEVA and N.A. USTYNYUK

Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilova St., 28, Moscow, 117813 (U.S.S.R.)

(Received August 15th, 1978)

Summary

Two novel methods are proposed for the synthesis of σ-ethynylmetal carbonyl derivatives. Firstly, reaction of metal carbonyl anions with haloacetylenes, and secondly, reaction of metal carbonyl anions with mixed ethynylphosphonium salts.

The former method gave a 40% yield of $C_5H_5(CO)_3CrC{\equiv}CC_6H_5$ for the first time. The latter method is prefered for the synthesis of $C_5H_5(CO)_3MC{\equiv}CC_6H_5$ (M = Mo, W) giving 45—54% of the σ-phenylethynyl derivatives.

Up until now the σ-ethynyl radical was introduced into a compound of a transition metal, with an appropriate ligand environment, mainly by reaction of the complex metal halides with metallic derivatives of acetylene, or via an oxidative addition of the acetylenic derivatives to the low oxidation state transition metal complexes. The great majority of σ-ethynyl-π-cyclopentadienyl transition metal compounds have been prepared by the former method. The latter method has been used most often for the synthesis of the Group VIII metal σ-ethynyl compounds. Other methods known are of more limited value [1]. In particular, the compounds $C_5H_5(CO)_3MC{\equiv}CR$ (M = Mo, W) have been obtained earlier by reaction of $C_5H_5(CO)_3MoCl$ with the respective Grignard reagents (M = Mo, R = n-C_4H_9, C_6H_5 [2]) or, in the case where R = C_6H_5, by decarbonylation of the respective σ-acyl derivatives, $C_5H_5(CO)_3MCOC{\equiv}CC_6H_5$ (M = Mo, W [3]).

Thus, one of the most common methods of synthesis of the metal carbonyl σ-derivatives, the reaction of metal carbonyl anions with haloacetylenes, has never been used for preparation of σ-ethynyl compounds. Obviously this may be explained by a commonly adopted viewpoint that nucleophilic substitution of halogen at an acetylenic carbon is hindered to the same extent as at an ethylenic one. Such concepts can be found in the well-known textbooks and monographs. For example: "the haloacetylenes, in turn, fail to give many of the characteristic substitution reactions common to the alkyl and aryl halides and in consequence are of little use in further synthesis" [4], also, "the haloacetylenes, such as $RC{\equiv}C{-}Cl$, possess similar (to vinyl halides *) inertness in S_N1 and S_N2 reactions" [5].

However, within the last fifteen years a number of reactions have been reported for haloacetylenes and nucleophiles which resulted in a nucleophilic substitution of an acetylenic halogen sometimes at a rate exceeding that of the halogen substitution at an sp^3 carbon atom. Reactions of this type and modern concepts on their mechanisms are summarised in ref. 6.

Thus, on the basis of literature data the metal carbonyl anion reactions with haloacetylenes could be assumed to produce the corresponding ethynyl compounds. To check this hypothesis, within our studies of the compounds $C_5H_5(CO)_3MC{\equiv}CR$ [3], we investigated the reactions of $[C_5H_5(CO)_3M]^-[K]^+$ (I, M = Cr; II, M = Mo; III, M = W) with phenylbromoacetylene (IV). Solutions of metal carbonyl anions I—III and IV were mixed in THF at —70° C and the reaction mixture was slowly warmed to room temperature. At this moment IR spectra and TLC showed the absence of the starting anions in the reaction mixture and the formation of phenylethynyl derivatives V—VII and bromides VIII—X as the main products (eq. 1).

$$\begin{array}{ccccccc} [C_5H_5(CO)_3M]^-[K]^+ & + & C_6H_5C{\equiv}CBr & \rightarrow & C_5H_5(CO)_3MC{\equiv}CC_6H_5 & + & C_5H_5(CO)_3MBr \\ (\mathrm{I\ M = Cr} & & (\mathrm{IV}) & & (\mathrm{V\ M = Cr} & & (\mathrm{VIII\ M = Cr} \\ \mathrm{II\ M = Mo} & & & & \mathrm{VI\ M = Mo} & & \mathrm{IX\ M = Mo} \\ \mathrm{III\ M = W}) & & & & \mathrm{VII\ M = W}) & & \mathrm{X\ M = W}) \end{array} \tag{1}$$

This reaction is the most preparative using the chromato anion I. In this case σ-phenylethynyl compound V, until now unreported, is the single isolated product (40%), apparently due to decomposition of the unstable bromide VIII [7] during chromatography. In the case of tungstate and molybdate anions, III and II, a mixture of σ-phenylethynyl- (VI, VII) and bromo derivatives (IX, X) are obtained in comparable quantities. By means of chromatography and subsequent fractional crystallization we succeeded only in partial separation of these components. Approximate estimation shows that the yield of VI—VII (24—28%) is greater than that of bromides IX and X.

On the basis of the data available it is impossible to suggest a mechanism for the reaction of anions I—III with IV without the evidence from additional investigations. The results of such a study and reactions of I—III and other metal carbonyl anions with a large number of haloacetylenes will be reported later.

Since compounds VI and VII could not be completely isolated in reactions of II and III with IV we used another approach for their synthesis, the reaction of II and III with phenylethynyltriphenylphosphonium bromide (XI). The choice of XI as phenylethynylating agent was determined by the following considerations: it is known that the arylating ability of tetraphenylphosphonium salts is lower than that of triphenylsulfonium and diphenyliodonium salts;

---

* Our remark.

$(C_6H_5)_4P^+$ may arylate successfully only the highly nucleophilic cyclopentadienyl dicarbonyl ferrate anion [8]; in the case of other metal carbonyl anions the reaction results only in the exchange of K^+ or Na^+ cations with phosphonium cation [8]. Diphenyliodonium and triphenylsulfonium salts arylate in high yield the less nucleophilic anions $[C_5H_5(CO)_3M]^-[Na]^+$ (M = Mo, W) [9—11]. There are no examples of the use of onium compounds for the introduction of the ethynyl groups into transition metal compounds. The totally symmetric ethynyl iodonium, sulfonium or phosphonium salts are unknown. Only the mixed salts $[C_6H_5C{\equiv}C{-}I{-}C_6H_5]^+[Cl]^-$ [12] and $[C_6H_5C{\equiv}C{-}P(C_6H_5)_3]^+[X]^-$ (X = Cl, Br) are described [12]. The mixed phenylethynyl iodonium salts react with nucleophilic agents under milder conditions when compared to the reaction of diphenyliodonium salts and in these reactions the phenylethynyl radical (not phenyl) is combined with the nucleophile [12]. One could suggest that the same is true for mixed phosphonium salts and the salts of type XI would be suitable ethynylating agents. Their reactions with metal carbonyl anions would proceed more readily than similar interactions with tetraphenylphosphonium salts and lead to σ-phenylethynylmetal carbonyl derivatives.

Anions I—III react with $[C_6H_5C{\equiv}CPPh_3]Br$ with differing ease. For example, the reaction of tungstate anion III with XI proceeds to completion at 25° C and gives $C_5H_5(CO)_3WC{\equiv}CC_6H_5$ (45%), $(C_6H_5)_3P$ (70%) and $[C_5H_5(CO)_3W]_2$ (traces) (eq. 2). Such a synthesis of VII is more advantageous than the decarbonylation of $C_5H_5(CO)_3WCOC{\equiv}CC_6H_5$ [3], and the reaction described above of III with IV, since the yield of VII is higher and the bromide X, which hinders the separation of VII, is absent.

$$\underset{\text{(III)}}{[C_5H_5(CO)_3W]^-[K]^+} + \underset{\text{(XI)}}{[C_6H_5C{\equiv}CPPh_3]Br} \rightarrow$$

$$\underset{\text{(VII)}}{C_5H_5(CO)_3WC{\equiv}CC_6H_5} + [C_5H_5(CO)_3W]_2 + P(C_6H_5)_3 \qquad (2)$$

The reaction of molybdate anion II with XI in THF, requires heating to 40—45°C for its completion, giving the phenylethynyl derivative VI (54%). Besides VI, 8% of the mixture of *cis*- and *trans*-isomers of $C_5H_5(CO)_2Ph_3PMoBr$ (XII) and traces of $[C_5H_5(CO)_3Mo]_2$ were isolated. Short refluxing in THF (0.5 h) yielded, besides VI and XII as the main products, also some amount of the light yellow hydride $C_5H_5(CO)_2Ph_3PMoH$ (XIII) and a red product, m.p. 158° C, showing the carbonyl IR vibration bands at 1845, 1920 and 1990 cm^{-1} (KBr pellet); its structure is under study. Formation of the phosphine substituted complexes XII and XIII may be due to reaction of preliminary generated $C_5H_5(CO)_3MoBr$ and $C_5H_5(CO)_3MoH$ with triphenylphosphine. The yield of the phosphine-containing products is enhanced with increasing temperature.

Unlike compounds II and III, the chromate anion I cannot be ethynylated with $[C_6H_5C{\equiv}CPPh_3]Br$. The IR spectrum shows that the reaction terminates by formation of the salt $[C_5H_5(CO)_3Cr]^-[C_6H_5C{\equiv}CPPh_3]^+$ and does not proceed further when heated to 100° C in ethereal solvents. Higher temperatures cause only a decomposition. Thus, the ease of reactions of anions I—III with $[C_6H_5C{\equiv}CPPh_3]Br$ agrees qualitatively with their nucleophilic character: C_5H_5-

$(CO)_3W^- > C_5H_5(CO)_3Mo^- > C_5H_5(CO)_3Cr^-$ [14].

On the basis of data available it is not possible to draw firm conclusions about the reaction mechanism of metal carbonyl anions I—III with the phosphonium salt XI. One may assume the formation of phosphoranes, $C_5H_5(CO)_3$-M—$PPh_3(C{\equiv}CC_6H_5)$, analogous to the scheme proposed for reaction of $[C_5H_5(CO)_2Fe^-][K]^+$ with $[P(C_6H_5)_4]^+$ [8]. Thus, reactions of metal carbonyl anions with mixed ethynylphosphonium salts, or with haloacetylenes, are new methods of synthesis of σ-ethynylmetal carbonyl derivatives. They offer advantages for the synthesis of $C_5H_5(CO)_3MC{\equiv}CC_6H_5$ compounds over those employed earlier [2,3] and supplement each other. In these methods the composition of the reaction products is determined by the nature of the metal (metal carbonyl anion nucleophilicity) and reaction conditions.

Phenylethynyl derivatives V—VII are yellow crystalline solids which melt above 100° C, are stable in air when solid and slowly decompose in solution. We are now investigating their thermolysis and reactions with some *n*-donors and electrophiles. The results will be reported in future communications.

Experimental

With the exception of preparative TLC all operations were performed under purified argon. Silica gel L 100/160 (ČSSR) was used for chromatography. The IR spectra were recorded on a UR-20 spectrophotometer. The PMR spectra were recorded on a Perkin—Elmer R-12 spectrometer with hexamethyldisiloxane as internal standard. If not specified the values of chemical shifts and $\nu(C{\equiv}O)$ are given for $CDCl_3$ and $CHCl_3$ solutions, respectively. The frequencies of triple bond stretching vibrations are obtained from the IR spectra in KBr pellets. Phenylethynyltriphenylphosphonium bromide was prepared by a literature method [15].

(1) $C_5H_5W(CO)_3K$ (III) and $C_6H_5C{\equiv}CBr$ (IV)

1.77 g (0.011 gmol) of IV was added, at —70° C, to a filtered solution of III, obtained from 4.33 g (0.005 gmol) of $[C_5H_5W(CO)_3]_2Hg$ and 0.8 ml of K/Na alloy in 75 ml of THF. The reaction mixture was gradually warmed to room temperature. The solution was evaporated in vacuo, the residue dissolved in benzene and chromatographed on a silica gel column (30 × 3 cm). Elution was by petroleum ether followed by petroleum ether/benzene mixtures with a gradual increase in benzene content and finally with pure benzene. The maroon, yellow and orange fractions were collected in their order of elution. From the maroon fraction 0.09 g (2.7%) of dimer $[C_5H_5W(CO)_3]_2$ was obtained. From the yellow fraction 1.21 g of a mixture of VII (main product), dimer $[C_5H_5W(CO)_3]_2$ and X were isolated. From the orange fraction 0.79 g of mixture of X (main product) and VII was isolated. TLC of these mixtures on silica gel in different mixtures of petroleum ether and benzene failed to separate VII and X. Small amounts of pure yellow VII were isolated by fractional reprecipitation from benzene solution with heptane VII precipitated first (its IR spectrum and R_f were identical with those of a sample prepared in *4*), further evaporation afforded the mixture of VII and X. Yields of VII and X were approximately 28 and 19%, respectively.

(2) $C_5H_5Mo(CO)_3K$ (II) and IV

The preparation was carried out as for *1* starting from 3.45 g (0.005 gmol) $[C_5H_5Mo(CO)_3]_2Hg$, 0.6 ml K/Na alloy and 1.77 g of IV in 100 ml of THF. After evaporation of THF the residue was dissolved in benzene and chromatographed on silica gel plates in (1/1) benzene/petroleum ether. The upper maroon band, with traces of the dimer $[C_5H_5Mo(CO)_3]_2$, was discarded. The yellow and orange bands did not separate. 0.85 g of VI (24%) (identical with a sample obtained earlier [3]) was isolated from the yellow band. 0.39 g (12%) of IX, with VI as an impurity, was obtained from the orange band by fractional reprecipitation.

(3) $C_5H_5Cr(CO)_3K$ (I) and $C_6H_5C{\equiv}CBr$ (IV)

The method was analogous to *1*, starting from 3.01 g (0.005 gmol) of $[C_5H_5Cr(CO)_3]_2Hg$, 0.6 ml of K/Na alloy and 1.67 g (0.01 gmol) of IV in 100 ml of THF. After evaporation of THF the residue was dissolved in benzene and chromatographed on a silica gel column (30 × 3 cm) in benzene. Elution was by benzene, the yellow fraction was separated and collected. The solution was concentrated and heptane added. The yellow-green solid precipitated, was filtered off and washed with cold pentane. 1.2 g of V (40% per $[C_5H_5Cr(CO)_3]_2$-Hg) was obtained. M.p. 117—118°C (heptane); $\nu(C{\equiv}O)$ 1960, 2040, $\nu(C{\equiv}C)$ 2110 cm^{-1}; $\delta(C_5H_5)$ 5.45 (s), $\delta(C_6H_5)$ 7.47—7.32 ppm (acetone-d_6). (Found: C, 62.91; H, 3.49; Cr, 17.00. $C_{16}H_{10}CrO_3$ calcd.: C, 63.58; H, 3.33; Cr, 17.21%).

(4) $C_5H_5W(CO)_3K$ (III) and $[(C_6H_5)_3PC{\equiv}CC_6H_5]Br$ (XI)

3.5 g (0.008 gmol) of XI was added to the filtered solution of III (prepared by reduction of 3.42 g (0.004 gmol) of $[C_5H_5(CO)_3W]_2Hg$ with K/Na alloy (0.41 ml) in 75 ml of THF) with stirring and cooling to −30°C. The reaction mixture was slowly warmed to room temperature. The course of the reaction was followed by referring to the IR spectra of the mixture. The starting anion was already absent in the reaction mixture at room temperature. The solvent was evaporated in vacuo, the residue dissolved in benzene and chromatographed on silica gel plates in benzene. The upper red band, with traces of $[C_5H_5W(CO)_3]_2$, was discarded. The middle yellow band gave 1.64 g (45%) of VII, m.p. 142—143°C (benzene/heptane). $\nu(C{\equiv}O)$ 1950, 2040 cm^{-1}, $\nu(C{\equiv}C)$ 2110 cm^{-1}. $\delta(C_5H_5)$ 5.76 (s), $\delta(C_6H_5)$ 7.53—7.07 ppm. (Found: C, 44.56, 44.83; H, 2.33, 2.39; W, 42.20, 41.90. $C_{16}H_{10}O_3W$ calcd.: C, 44.26; H, 2.32; W, 42.36%.)

(5) $C_5H_5Mo(CO)_3K$ (II) and XI

3.15 g (0.0071 gmol) of XI was added, with stirring, at room temperature to the filtered solution of II, prepared analogously to III from 2.45 g (0.0036 gmol) of $[C_5H_5Mo(CO)_3]_2Hg$ and 0.4 ml of K/Na alloy in 100 ml of THF. The reaction mixture was heated to 40—50°C for 2 h until no more $C_5H_5Mo(CO)_3$ anion was present (from IR spectra). After cooling to room temperature the solvent was evaporated in vacuo, the residue dissolved in benzene and chromatographed on silica gel plates in 1/1 benzene/petroleum ether. The upper maroon band containing $[C_5H_5Mo(CO)_3]_2$ and $[C_5H_5Mo(CO)_3]_2Hg$ was discarded. From the middle yellow band 1.33 g (54%) of VI was obtained, m.p. 118—120°C (benzene/heptane), $\nu(C{\equiv}O)$ 1967, 2047 cm^{-1} (its IR spectrum and R_f are identical to those of a sample prepared earlier [3]). From the lower bright red band 0.33 g (8%) of $C_5H_5Mo(CO)_2P(C_6H_5)_3Br$ was obtained, $\nu(C{\equiv}O)$ 1890, 1980 cm^{-1} (from IR spectrum and R_f it is identical with an authentic sample of $C_5H_5Mo(CO)_2P(C_6H_5)_3Br$).

References

1 L.P. Yur'eva, in "Metody elementoorganicheskoi khimii, π-kompleksy perekhodnykh metallov s dienami, arenami, soedineniya s σ-svyaz'yu M-C", Nauka Publ., Moscow, 1976, Ch. 4.
2 M.L.H. Green and T. Mole, J. Organometal. Chem., 2 (1964) 15.
3 A.N. Nesmeyanov, L.G. Makarova, V.N. Vinogradova and N.A. Ustynyuk, Izv. Akad. Nauk SSSR, Ser. Khim., in press.
4 J.A. Newland and R.A. Vogt, The Chemistry of Acetylene, New York, 1945, p. 71.
5 J.D. Roberts and M.C. Caserio, Basic Principles of Organic Chemistry, New York, Amsterdam, 1964, p. 321.
6 S.L. Miller and J.I. Dickstein, Acc. Chem. Res., 9 (1976) 358.
7 A.R. Manning and D.I. Thornhill, J. Chem. Soc. A, (1971) 637.
8 J.E. Ellis, J. Organometal. Chem., 111 (1976) 331.
9 A.N. Nesmeyanov, Yu.A. Chapovskii, B.V. Lokshin, A.V. Kisin and L.G. Makarova, Dokl. Akad. Nauk SSSR, 171 (1966) 637.
10 A.N. Nesmeyanov, Yu.A. Chapovsky, I.V. Polovyanyuk and L.G. Makarova, J. Organometal. Chem., 7 (1967) 329.
11 N.A. Ustynyuk, Dissertation, 1973, Moscow.
12 F.M. Beringer and S.A. Galton, J. Org. Chem., 30 (1965) 1930.
13 J.I. Dickstein and S.I. Miller, J. Org. Chem., 37 (1972) 2168.
14 R.E. Dessy, R.L. Pohl and R.B. King, J. Amer. Chem. Soc., 88 (1966) 5121.
15 H.G. Viehe and S.J. Delavarenne, Chem. Ber., 103 (1970) 1216.