

in which the second step is rate-determining, and with the observed $k = k_1 k_3 k_2^{-1}$. The analogous change from chromium(V) to chromium(IV), or its reverse, is also the slow step of the other reactions discussed, as well as the slow step in the chromium(III)–chromium(VI) exchange.⁸ The explanation for this behavior based on different coordination numbers (4 and 6, respectively) for the intermediates chromium(V) and chromium(IV) has been presented.^{6–8}

Further studies on the vanadium(IV)–chromium(VI) system are in progress in an attempt to push the range over which each reactant and product concentration is varied to the very limit of measurement to establish whether the present rate equation remains valid under all attainable concentrations or whether any of the other possible terms can become important. The effect of acid concentration, which was constant in all these experiments, is also under investigation.

(8) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2825 (1961).

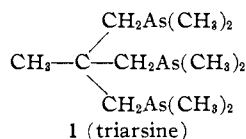
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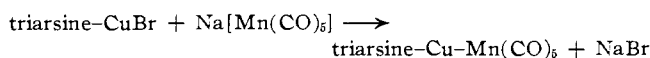
An Organometal Complex Containing a Copper–Manganese Bond

Sir:

Recent studies^{1,2} in these laboratories have yielded a number of compounds containing Au–M bonds (M = Mn, Fe, Co, and W). With a view to solving the more difficult problem of preparing compounds containing Cu–M and Ag–M linkages,³ we have synthesized the terdentate arsenic ligand **1** which readily forms complexes with the halides of copper(I), silver(I),



and gold(I). The copper complex, triarsine–CuBr, a monomeric nonelectrolyte evidently containing tetrahedrally coordinated copper(I), reacts with 1 equiv. of sodium pentacarbonylmanganate(–I)⁴ in tetrahydrofuran according to the following equation



Addition of petroleum ether (b.p. 60–80°) precipitates the yellow-brown product, which can be purified using a dichloromethane–petroleum ether mixture (yield 80%). *Anal.* Calcd. for C₁₆H₂₇O₅CuMn: C, 29.9; H, 4.2; As, 35.0; Cu, 9.9; Mn, 8.5; mol. wt., 642. Found: C, 30.2; H, 4.5; As, 34.7; Cu, 9.7; Mn, 8.2; mol. wt.,⁵ 618.

The compound is air-stable and diamagnetic. It is soluble in most common solvents, and in nitrobenzene it is a nonconductor. The infrared spectrum of the

(1) C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, in press.

(2) A. S. Kasenally, R. S. Nyholm, and M. H. B. Stiddard, *ibid.*, in press.

(3) Professor J. Lewis, *et al.* (University of Manchester, personal communication), have synthesized recently compounds of the type R–M–Mn(CO)₅, where M = Cu or Ag and R = tertiary phosphine or arsine.

(4) W. Hieber and G. Wagner, *Z. Naturforsch.*, **12b**, 478 (1957).

(5) Determined in dichloromethane using a Mechrolab vapor pressure osmometer.

compound in the C–O stretching region has been studied and shows two bands, at 2010 (ms) and 1891 (vs) cm.^{–1}.

Similar experiments starting with the silver(I) complex triarsine–AgBr indicate the formation of an analogous compound containing a Ag–Mn bond, but it is too unstable to be characterized.⁶ The triarsine reacts with gold(I) chloride to yield a product triarsine–(–AuCl)₃ in which the arsenic atoms coordinate independently to the gold atoms. This complex, on reaction with sodium pentacarbonylmanganate(–I), gives the expected product triarsine[–Au–Mn(CO)₅]₃.

We are investigating at present the preparation of similar complexes containing Cu–Fe and Cu–Co bonds; these investigations will be described at a later date.

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(6) However, by using the aromatic triarsine (*o*-Me₂As–C₆H₄)₂AsMe we have now synthesized the air-stable complex triarsine–Ag–Mn(CO)₅.

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The Wittig Reaction. I. Synthesis of β,γ-Unsaturated Acids

Sir:

The Wittig reaction has been used to prepare a variety of α,β-unsaturated acids or their esters from carbomethoxymethyltriphenylphosphonium halides.^{1–3} In their review on controlling the steric course of the Wittig reaction, Bergel'son and Shemyakin⁴ reported the preparation of eleven nonconjugated unsaturated fatty acids. However, no record of the preparation of the unconjugated β,γ-unsaturated acids by the Wittig reaction has come to our attention. Our examination of the literature has not revealed a single reaction or series of reactions which can be designated convenient for the preparation of this type of acid.

We wish to report that the Wittig reaction has been adapted to a versatile synthesis of β,γ-unsaturated acids. Another view of this application of the Wittig reaction is that it permits the lengthening of a carbon chain by three units in one step.

The required intermediate β-carboxyethyltriphenylphosphonium chloride (**1**) has been prepared according to the method of Denny and Smith.⁵ The phosphonium chloride (**1**) was obtained as a glass which crystallized upon trituration with acetone; **1** was recrystallized by dissolving in chloroform and diluting with acetone to give analytically pure product melting at 196–197°.

Since the preparation of the ylide (**3**) presumably would go through the intermediate phosphobetaine (**2**),⁵ the reaction has been examined only in dimethyl sulfoxide (DMSO) solution to avoid solubility problems. The usual Wittig procedure of first preparing

(1) G. Fodor and I. Tomoskozi, *Tetrahedron Letters*, 579 (1961).

(2) S. Trippett and D. M. Walker, *Chem. Ind. (London)*, 990 (1961).

(3) V. F. Kucherov, B. G. Kovalev, I. I. Nazarova, and L. A. Yanovskaya, *Izv. Akad. Nauk. SSSR, Old. Khim. Nauk.*, 1512 (1960); *Chem. Abstr.*, **55**, 1420b (1961).

(4) L. D. Bergel'son and M. M. Shemyakin, *Tetrahedron*, **19**, 149 (1963).

(5) D. B. Denny and L. C. Smith, *J. Org. Chem.*, **27**, 3404 (1962).