

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).

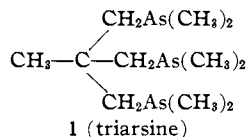
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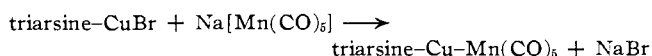
An Organometal Complex Containing a Copper–Manganese Bond

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 $\text{C}_{16}\text{H}_{27}\text{O}_5\text{CuMn}$: 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.

Acknowledgments.—We wish to thank the Ethyl Corporation for gifts of manganese carbonyl and E. I. Du Pont de Nemours Limited for financial support to A. S. K.

(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

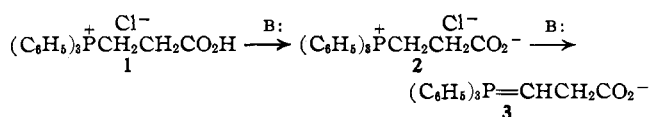
(1) G. Fodor and I. Tomoskozi, *Tetrahedron Letters*, 579 (1961).

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

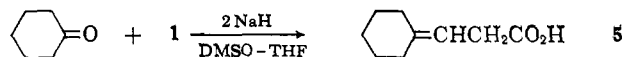
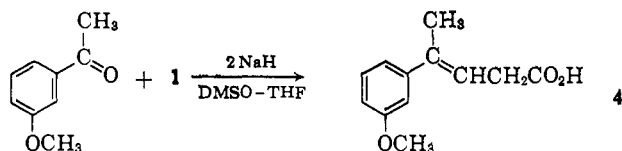
(3) V. F. Kucherov, B. G. Kovalev, I. I. Nazarova, and L. A. Yanovskaya, *Izv. Akad. Nauk. SSSR, Old. Khim. Nauk.*, 1512 (1960); *Chem. Abstr.*, **55**, 1420b (1961).

(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).



the intermediate ylide from the phosphonium halide⁶ gave only traces of desired acidic product. This is probably due to the elimination of triphenylphosphine to form acrylic acid. Yields of about 10% of 4-(*m*-methoxyphenyl)-3-pentenoic acid (**4**) were obtained sporadically when *m*-methoxyacetophenone was added to a solution of sodium methylsulfinylcarbanion⁷ prior to the addition of **1**. However, when equivalent quantities of the ketone and **1** were dissolved in 1:1 DMSO-tetrahydrofuran and added to dry sodium hydride under nitrogen at 0°, the yields increased to above 50%. This procedure has afforded crude **4** in the range of 53–69% yield with reaction times of 4 and 18 hr. The crude product has been recrystallized from cyclohexane to give **4**, melting at 86–87°. *Anal.* Found: C, 69.66; H, 6.62; neut. equiv., 206.



Cyclohexanone reacted with **1** to yield 66% of β -cyclohexylidenepropionic acid (**5**) as an amber liquid which was distilled over as short path [105° (0.35 mm.)] to give a clear crystalline solid (m.p. 37–39°). *Anal.* Found: C, 70.31; H, 9.45; neut. equiv., 158.

The structures of **4** and **5** were established by their n.m.r. spectra. The spectrum for **4** (m.p. 86–87°) showed a doublet for the methyl at 123 c.p.s. ($J = 1$ c.p.s.), which is appropriate for a methyl attached to a trisubstituted double bond with the proton on the adjacent olefinic carbon.⁸ There was a single olefinic proton which showed a triplet centered about 357 c.p.s. Only structure **4** fits this n.m.r. pattern.

The n.m.r. spectrum obtained for **5** was best interpreted in terms of the structure indicated. The two hydrogens in the position α to the carboxyl and adjacent to the double bond appeared as a doublet at 186 c.p.s. ($J = 7$ c.p.s.). The other four allylic hydrogens formed a band envelope at 128 c.p.s. There was one olefinic proton with a triplet at 315 c.p.s. The allylic proton pattern excluded the presence of an endocyclic double bond and the triplet of the olefinic proton showed that the isomeric β -cyclohexylacrylic acid was not present.

The melting range (58–72°) of crude **4** indicated that a mixture of isomers had been obtained. This was confirmed by gas-liquid chromatography (g.l.c. done in a 0.5 in. \times 5 ft. column of 1.5% SE-30 on Gas Chrom-2 in a Perkin-Elmer vapor fractometer, Model 154, at 156° and a helium flow setting of 120 on the rotameter) of the methyl esters, prepared by treatment of the acids with ethereal diazomethane, which showed

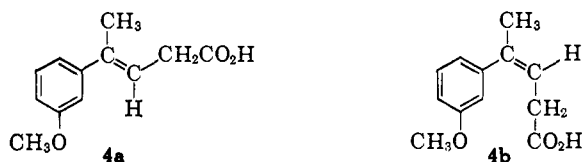
(6) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(7) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(8) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 85.

74–80% of the crude Wittig products to be in a peak with a retention time of 4.80–5.04 min. and 19–24% in a second peak at 2.90–3.02 min. Two or three minor components accounted for 1–2% of the mixtures. The g.l.c. of the ester of the microanalytical sample of crystalline **4** demonstrated that it was homogeneous and that it had the retention time of 4.80–5.04 min. Similar analysis of a liquid mixture recovered from recrystallization mother liquors showed that it contained predominantly the substance with the 2.90–3.02 min. retention time and also about 20% of the ester of the crystalline isomer. The n.m.r. spectra confirmed that the crystalline isomer and the predominant component of the noncrystalline mixture were geometric isomers.

Ultraviolet spectral comparison of the crystalline and noncrystalline products suggested that the crystalline **4** is *trans* [**4a**, λ_{max} 286 m μ (ϵ 2319)] and that the predominant component of the liquid mixture is *cis* [**4b**, λ_{max} 281 m μ (ϵ 2171)].⁹



Continuing studies have extended the scope of this application of the Wittig reaction to other carbonyl reactants and phosphonium halides. The β , γ -unsaturated acids are being investigated for themselves and as intermediates in further synthesis.

(9) Since both the λ_{max} and ϵ_{max} values of the crystalline isomer are greater than for the mixture in which the other isomer is predominant, we feel that the conclusion of C. N. R. Rao ("Ultraviolet and Visible Spectroscopy," Butterworths, Inc., London, 1961, p. 69) that the absorption intensities of long wave length bands of *trans* isomers are always greater than those of the corresponding *cis* isomers may be applied here. We feel justified in using ϵ_{max} for the mixture since, upon hydrogenation, it gave the single product 4-(*m*-methoxyphenyl)valeric acid (homogeneous by g.l.c.), also obtained from crude Wittig reaction products, and from the homogeneous crystalline isomer. It is our assumption that the interaction between the phenyl group and the carboxymethyl group would have a more pronounced effect upon the coplanarity of the double bond and the benzene ring than the interaction between the methyl and carboxymethyl.

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2-*exo,cis*-Bicyclo[3.3.0]octane Derivatives via Free-Radical Additions to *cis,cis*-1,5-Cyclooctadiene^{1,2}

Sir:

While ionic^{3,4} and carbene⁴ reactions of cyclic systems usually lead to transannular rearrangements, with the exception of bicyclo[2.2.1]heptadiene⁵ (a homoallylic system), analogous free-radical reactions are unknown. It has now been found that only 2-*exo,cis*-bicyclo[3.3.0]octane derivatives are formed by free-radical additions to *cis,cis*-1,5-cyclooctadiene.

(1) This work was supported in part by a research grant (GM 11499-01) from the National Institutes of Health.

(2) Complementary results are found in the work of R. Dowbenko, *J. Am. Chem. Soc.*, **86**, 946 (1964).

(3) E.g., A. C. Cope, J. N. Grisar, and P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 4299 (1960).

(4) (a) L. Friedman and H. Shechter, *ibid.*, **83**, 3159 (1961); (b) *ibid.*, ref. 5a-j.

(5) D. J. Trecker and J. P. Henry, *ibid.*, **85**, 3204 (1963); for a bibliography of such reactions, see ref. 3–8 contained therein.