FORMATION OF OXYGEN HETEROCYCLES FROM ALKYNES CATALYZED BY $Ru_3(CO)_{12}$

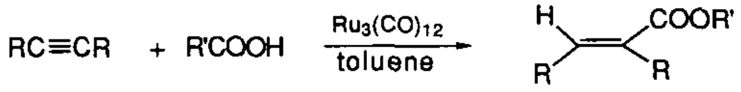
Naim Menashe and Youval Shvo*

School of Chemistry, Raymond and Beverly Sackler Faculty of
Exact Sciences
Tel Aviv University, Tel Aviv, 69978, Israel

Abstract - When dimethyl acetylenedicarboxylate and 2-cyanophenylphenylacetylene were each reacted with acetic acid under catalysis of $Ru_3(CO)_{12}$, 2,3,4-tricarbomethoxy-α-pyrone (**1**) and 3-phenylisocoumarin (**3**) were formed in good yields.

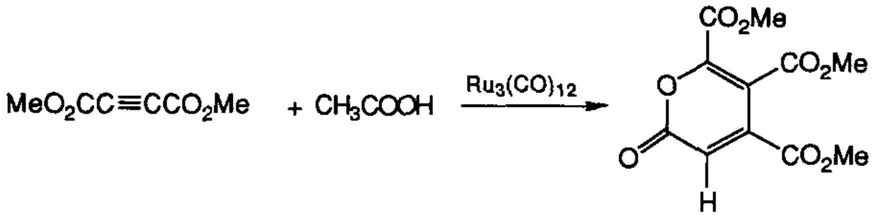
More than often, and sometimes totally unexpectedly, transition metal chemistry generates, in one step, molecular structures that otherwise demand considerable synthetic efforts by classical organic chemistry. It is not as simple matter to always predict the outcome of such reactions, but once demonstrated, they may provide a basis for new chemistry. Catalytic reactions are of special importance. On such a case, where the products are oxygen heterocycles, we would like to briefly report in the present communication.

In previous studies[1] we have developed a useful catalytic addition reaction of carboxylic acids to alkyne using $Ru_3(CO)_{12}$. The reaction has been found to be completely general inasmuch as all the combinations of structural different alkynes and carboxylic acids tested were found to be reactive. Equimolar quantities of alkyne and acid in toluene solution containing 2% mole of $Ru_3(CO)_{12}$ have been used according to the following equation:



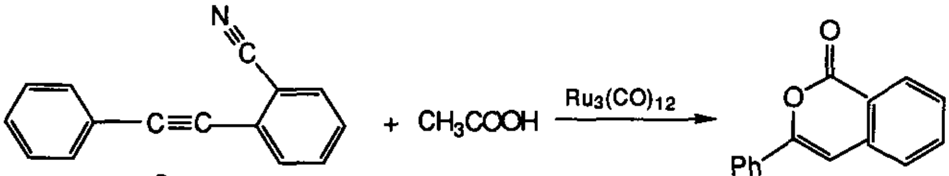
In the present study we have carried out such reactions but using now a carboxylic acid (liquid) as the solvent. Two structurally different alkynes have been studied that gave rise, unexpectedly, to heterocyclic compounds.

The first alkyne, dimethyl acetylenedicarboxylate (3.55 g, 25 mmol), acetic acid (9.0 g, 150 mmol) and $Ru_3(CO)_{12}$ (105.6 mg, 0.165 mmol) were refluxed for 45 min. Following the appropriate work-up of the reaction mixture there was obtained 1.68 g (50%) of a crystalline material, mp 128 °C, for which structure (**1**), an α-pyrone derivative, has been assigned.[2] The reaction mixture was found to contain also dimethyl α-acetoxymaleate. The latter, when treated, in a separate experiment, with an equimolar quantity of dimethyl acetylenedicarboxylate in acetic acid but in the *absence* of the catalyst, failed to yield **1**. This implies that the dimerization step, as well as the addition reaction of the acid to the alkyne, must be metal assisted. However, little is presently known about the mechanism of this reaction.



1

In the second reaction, 2-cyanophenylphenylacetylene[3] **(2)** when treated as above, but for 12 h, gave 3-phenylisocoumarin **(3)** in 66% yield, mp 88 °C (lit.,[4] 88-89 °C) after crystallization from methylene chloride-pet. ether. No reaction occurred in the absence of the catalyst. Monitoring the reaction with gc analyses revealed the presence of several signals which eventually converged to that of **3**.



2 **3**

Spectral data,[5] elemental analysis and mp of the isolated crystalline material were found to be in accord with structure **(3)**.

Mechanistic studies are presently underway. Nevertheless, it has been established that water is not involved in the above reactions, and that the vinyl oxygen atom in both **1** and **3** originates from the acetic acid.

The above reactions proceed also in the presence of formic instead of acetic acid. It is therefore believed that they are a part of a general reactivity scheme associated with our recent discovery[6] that alkyne hydrocarbons react with dry formic acid (*no* catalyst) generating CO and hydration products of the alkynes.

A comprehensive report of our results will be published elsewhere.

REFERENCES

[1] M. Rotem and Y. Shvo, Organometallics, 1983, **2**, 1689; M. Rotem, I. Goldberg, U. Shmueli, and Y. Shvo, J. Organomet. Chem., 1986, **314**, 185; M. Rotem and Y. Shvo, J. Organomet. Chem., in press.

[2] Elemental analysis, ^{1}H-nmr, ^{13}C-nmr, and ms results are in accord with structure (**1**).

[3] L. Cassar, J. Organomet. Chem., 1975, **93**, 253.

[4] R. Charubbala, A. Guggisberg, M. Hesse, and H. Schmid, Helv. Chem. Acta, 1974 , **57**, 1096.

[5] ^{1}H-Nmr ($CDCl_3$) δ 6.87 (s, 1H), 7.30-7.86 (m, 8H), 8.23 (d, J = 8Hz, 1H). ^{13}C-Nmr ($CDCl_3$) δ 162.2 (C=O), 153.4 (O-C=), 101.6 (HC=), 134.2, 129.7, 129.3, 128.6, 127.9, 125.8, 125 (aromatic **C**H atoms), 137.3, 120.4, 120.3 (quaternary aromatic C atoms). Ir ($CHCl_3$) 1732 (C=O), 1638 (C=C) cm^{-1}. Ms m/z 222 (M^+,100%), 194 (13%), 118 (38%).

[6] N. Menashe, D. Reshef, and Y. Shvo, J. Org. Chem., 1991, **56**, 2912.

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