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AN EFFICIENT SYNTHESIS OF 3,4-DIOXOCYCLOBUTENECARBOXYLATE DERIVATIVES

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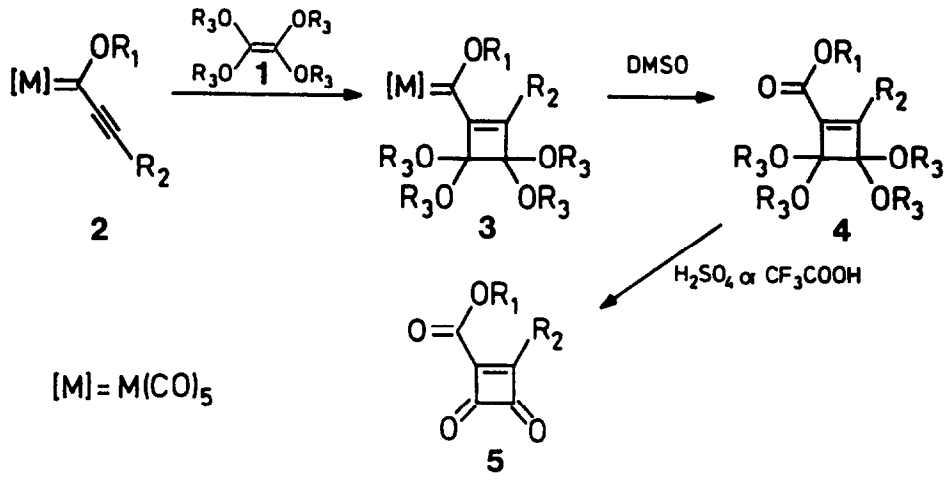
Abstract.- Alkynylalkoxycarbene metal complexes react readily with tetraalkoxyethylenes to give the corresponding [2 + 2] cycloadducts in high yields. From these adducts the title compounds were obtained by DMSO oxidation and final hydrolysis of the acetal groups.

Coordination to transition metals is one of the most powerful synthetic tools to enhance and/or change the chemical reactivity of organic compounds. In this context, transition metal carbene complexes are particularly valuable for promoting one pot formal multistep processes or otherwise not allowed reactions, due to their role as templates and/or modifiers of chemical behaviour on the nearby functionalities.[1]

We report herein how we took advantage of the electronic changes imposed by metal coordination on the triple bond of the conjugated alkynylcarbene moiety (high polarization and electron deficiency) to develop an efficient method for the preparation of 3,4-dioxocyclobutenecarboxylate derivatives which are of potential interest in bioorganic chemistry, advanced materials sciences as well as appreciated starting materials in organic synthesis.[2,3]

When tetraalkoxyethylene was reacted with different alkynylalkoxycarbene complexes of Cr and W under mild conditions the corresponding [2 + 2] cycloadducts were obtained in excellent yields (Table). In sharp contrast to our previous results from analogous reactions of these carbene derivatives with ethyl 3,3-diethoxyacrylate, whose adducts suffer a fast conrotatory opening to give mainly 2H-pyranylidenemetal complexes,[4] the corresponding tetraalkoxycyclobutenylalkoxycarbene complexes displayed a fair stability towards acetal hydrolysis[5] as well as acid or metal promoted ring opening.[6,7]

In a typical experiment 1 mmol of the appropriate carbene complex 2 was stirred with excess of olefin 1 as the reaction solvent, until T.L.C. control showed no starting complex (from 15 minutes to several hours). Flash column chromatography (hexane:diethyl ether 95:5) afforded pure complex 3 as red crystalline material after solvent removal. Further release of the organic ligand from the metal was achieved by mild DMSO oxidation (tenfold excess in diethyl ether at room temperature for 16 hours) and the solution was quickly filtered through a short silica gel column to remove the remaining thioether complex. The eluate was concentrated and the DMSO removed by vacuum evaporation to give 4 or, alternatively, the residue was transformed into the final dione 5 by treatment with trifluoroacetic acid (5a and 5c) or concentrated sulfuric acid (5b).[5,8]



TABLE[9]

	R_1	R_2	R_3	M	Time	3 Yield(%)	4 Yield (%)	5 Yield (%)
a	Me	n-Pr	Et	Cr (W)	15 min.	65 (60)	93 (91)	68 (61)
b	Et	Ph	Me	Cr	10 hr.	82	94	98
c	Me	Me_3Si	Me	W	12 hr.	78	95	92

It is remarkable that regardless of the nature of the triple bond substituents cyclobutendiones were the only products isolated in this reaction and the differences in reaction time can be attributed to steric effects. Although tetraalkoxyethylenes are reported to react with a variety of electron deficient ketenes[8,10] and activated olefins,[11] we could not detect any sign of cycloaddition when methyl 2-butynoate and tetraalkoxyethylene were kept under the mentioned reaction conditions. Slow olefin degradation was the only result instead. In the present reactions, the driving force can be brought about by the strong triple bond polarization due to the carbene-metal activation. Therefore, for cycloaddition purposes alkynyl alkoxymetalcomplexes can be envisaged as "activated acetylenes" no matter which is the nature of the substituent.

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5. Although severe acidic conditions were not tried (P.H.J. Ooms, J.W. Scheeren, R.J.F. Nivard. *Synthesis* 1975, 639) all complexes could be purified by column chromatography through silica gel without significant decomposition.

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9.- For
3a(W). IR ($CHCl_3$) 2070, 1990, 1947 cm^{-1}.
^1H NMR ($CDCl_3$) δ: 4.5 (s,3H), 3.9-3.1, (m,8H) 2.22 (t,J=7Hz,2H), 1.7-1.2 (m,2H), 1.19 (t,J=8Hz,6H), 1.18 (t,J=8Hz,6H), 0.9 (t,J=7Hz,3H).
^{13}C NMR ($CDCl_3$) δ : 319.0, 206.5, 197.8, 158.2, 142.0, 109.9, 106.9, 69.7, 60.6, 60.0, 30.4, 21.8, 15.8, 15.5, 14.7

4a. IR ($CHCl_3$) 1720, 1630 cm^{-1}.
^1H NMR ($CDCl_3$) δ : 4.1-3.5 (m,8H), 3.77 (s,3H), 2.52 (t,J=7Hz,2H), 1.9-1.4 (m,2H), 1.23 (t,J=7Hz,12H), 0.98 (t,J=7Hz,3H).

^{13}NMR ($CDCl_3$) δ : 165.6, 163.0, 135.2, 106.4, 59.6, 58.9, 51.1, 29.95
29.4, 20.5, 15.2, 14.3

5a. IR ($CHCl_3$) 1790, 1720, 1605 cm^{-1}.
^{1}H NMR ($CDCl_3$) δ : 3.97 (s,3H), 2.97 (t,J=8Hz,2H), 1.5-1.2 (m,2H), 0.9 (t,J=8Hz,3H).

3b. IR ($CHCl_3$) 2065, 1990, 1955 cm^{-1}.
^{1}H NMR ($CDCl_3$) δ: 7.5-7.3 (m,5H), 4.5 (q,J=7Hz,2H), 3.5 (s,6H), 3.38 (s,6H), 1.42 (t,J=7Hz,3H).
^{13}C NMR ($CDCl_3$) δ: 341.8, 225.2, 216.2, 151.5, 132.4, 131.9
129.2, 128.8, 127.8, 110.7, 106.8, 76.0, 52.7, 51.5, 14.6.
MS: m/e M 498 Other important peaks 358 (M -5 CO)

4b. IR ($CHCl_3$) 1710, 1635 cm^{-1}
^{1}H NMR ($CDCl_3$) δ : 7.85-8 (m,2H), 7.45-7.3 (m,3H), 4.28 (q,J=7Hz,2H), 3.55 (s,6H), 3.42 (s,6H), 1.3 (t,J=7Hz,3H).
^{13}C NMR ($CDCl_3$) δ: 162.7, 156.8, 133.9, 131.3, 130.3, 129.7.
128.0, 107.8, 107.3, 60.8, 52.3, 14.1.
M = 322. 1415 (Calcd. 322.1416).

5b. IR ($CHCl_3$) 1795, 1720, 1600, 1585 cm^{-1}.
^{1}H NMR ($CDCl_3$) δ : 8.6-8.4 (m,2H), 7.85-7.3 (m,3H), 4.55 (q,J=9Hz,2H), 1.43 (t,J=9Hz,3H)
^{13}C NMR ($CDCl_3$) δ : 197.7, 191.7, 189.7, 177.3, 160.2, 135.9, 131.3,
129.3, 126.9, 62.6, 14.0

3c. IR ($CHCl_3$) 2080, 1990, 1950 cm^{-1}.
^{1}H NMR ($CDCl_3$) δ : 4.5 (s,3H), 3.4 (s,6H), 3.3 (s,6H), 0.15 (s,9H).
^{13}C NMR ($CDCl_3$) δ : 318.4, 204.4, 197.0, 140.4, 129.4, 110.8, 108.9, 68.6, 51.7, 51.4, -0.3.

4c. IR ($CHCl_3$) 1725 cm^{-1}.
^{1}H NMR ($CDCl_3$) δ : 3.78 (s,3H), 3.49 (s,6H), 3.43 (s,6H) 0.27 (s,9H).
^{13}C NMR ($CDCl_3$) δ : 170.2, 163.3, 117.7, 109.0, 108.1, 52.1, 51.8, 51.6, -1.1
M = 304.1336 (Calcd. 304.1342)
Complexes 3a, 3b, 3c gave satisfactory elemental analysis.

5c. IR ($CHCl_3$) 1790, 1730 cm^{-1}.
^{1}H NMR ($CDCl_3$) 3.95 (s,3H), 0.4 (s,9H)

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