Nickel(0)-catalysed Novel Co-oligomerization of Ethoxy(trimethylsilyl)ethyne with Carbon Dioxide to 4,6-Diethoxy-3-[1-ethoxy-2,2-bis(trimethylsilyl)vinyl]-5-(trimethylsilyl)-2-pyrone

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A nickel(0) catalyst, which was generated from bis(cyclo-octadiene)nickel and bis(diphenylphosphino)butane, effected a novel co-oligomerization of three molecules of ethoxy(trimethylsilyl)ethyne with one molecule of carbon dioxide to afford the title compound (2) in an excellent yield.

Development of transition metal-catalysed efficient CO_2 fixation into unsaturated hydrocarbons is an important topic.[1] The nickel(0)-catalysed cycloaddition of two molecules of a monoacetylenic compound with one molecule of CO_2 to give a 2-pyrone is well known.[2] Here we report a novel nickel(0)-catalysed co-oligomerization of three molecules of ethoxy-(trimethylsilyl)ethyne (1) with CO_2 to give the pyrone (2) (Scheme 1).

When (1) was treated with CO_2 under pressure in tetrahydrofuran (THF) at 60 °C in the presence of a nickel(0) catalyst (10 mol%), generated from $Ni(cod)_2$ (cod = cyclo-octa-1,5-diene) and bis(diphenylphosphino)butane (dppb; 1 equiv.), (2) was obtained regiospecifically in excellent yield

(Table 1).† In the absence of dppb oligomerization of (1) occurred to produce 1,3,5-triethoxy-2,4,6-tris(trimethylsilyl)benzene and 1,2,4-triethoxy-3,5,6-tris(trimethylsilyl)-

**Table 1.** Nickel(0)-catalysed cycloaddition of ethoxy(trimethylsilyl)-ethyne (1) with CO_2 (Scheme 1).[a]

Ligand (L)	$L/Ni(cod)_2$	% Yield of 2-pyrone (2)[b]
$P(C_8H_{17}\text{-n})_3$	2	30
PPr^i_3	2	9[f]
dppe[d]	1	8[f]
dppp[e]	1	Trace
dppb	0.5	52[f]
	1	90 (80)[c]
	2	56

[a] (1), 0.50 mmol; $Ni(cod)_2/(1)$, 0.10; CO_2 (initial pressure at room temperature), 50 kg/cm²; solvent, THF (20 ml); temperature, 60 °C; time, 20 h. [b] Yield was determined by GC. [c] Value in parenthesis is isolated yield by PLC. [d] Bis(diphenylphosphino)ethane. [e] Bis(diphenylphosphino)propane. [f] Formation of the acetylene trimers 1,3,5-triethoxy-2,4,6- and 1,2,4-triethoxy-3,5,6-tris(trimethylsilyl)-benzenes was observed.
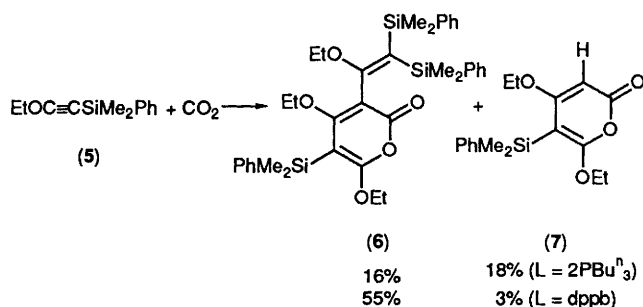

$$3\ EtOC{\equiv}CSiMe_3\ +\ CO_2\ \longrightarrow$$

(1)

(2)
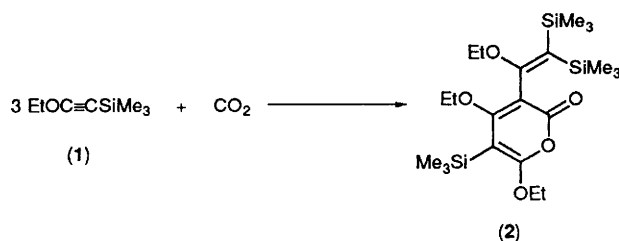
Scheme 1. *Reagents*: $Ni(cod)_2$–dppb.

† All new compounds have been fully characterized spectroscopically and their elemental composition has been determined by high-resolution mass spectroscopy.
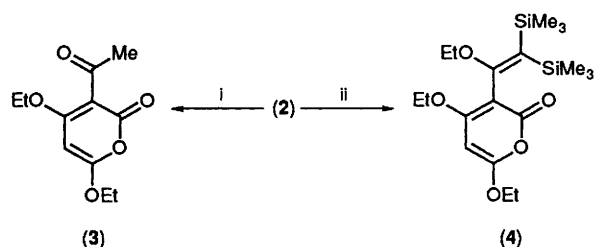
Scheme 2. *Reagents and conditions*: i, p-MeC$_6$H$_4$SO$_2$H, H$_2$O–MeCN, room temp., 20 h; ii, Bu$_4$NF, THF, 0 °C, 3 min.

Scheme 3. *Reagents and conditions*: Ni(cod)$_2$–L, THF, 60 °C, 20 h.

(a)

(b)

Figure 1. ORTEP drawings of (2) from two directions.

benzene. The structure of the tertiary phosphine ligand was crucial for the formation of (2), dppb being the most effective. Monodentate trialkylphosphines[3] were less effective. 1-(2-Pyridyl)-2-(di-n-butylphosphino)ethane, which is an efficient ligand in the nickel(0)-catalysed cycloaddition of diynes with CO$_2$ to give bicyclic 2-pyrones,[4] was ineffective. The Ni(cod)$_2$–dppb catalyst did not produce a 2-pyrone product from 1-(trimethylsilyl)hex-1-yne and CO$_2$. This finding and the formation of 4,6-diethoxy-2-pyrone[2c] from ethoxyethyne and CO$_2$ indicate that both ethoxy and trimethylsilyl groups play a decisive role in the formation of (2).

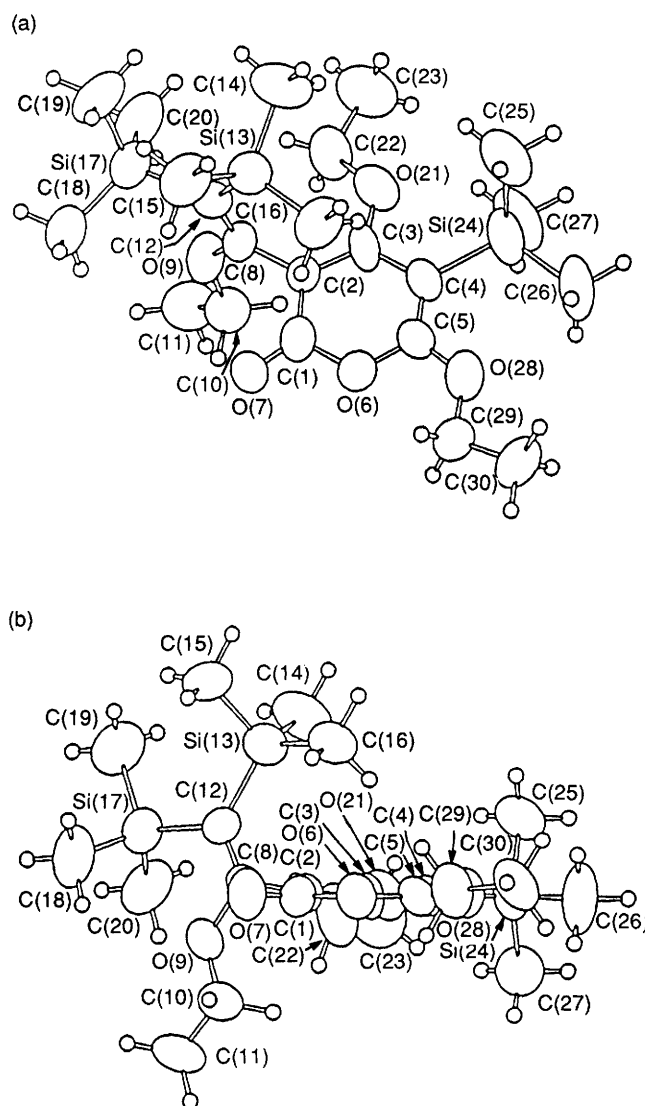An assignment of the structure of (2) was impossible by simple spectroscopic means. Its structure was determined by X-ray diffraction analysis (Figure 1).‡ The most interesting

structural feature of (2) is that the C-3 vinyl substituent is not coplanar with the 2-pyrone ring; the carbon–carbon double bond of the vinyl group is almost perpendicular to the ring plane [Figure 1(b)]. Noncoplanarity of the vinyl substituent with the 2-pyrone ring reduces the strong repulsion with the adjacent 4-ethoxy group.

The silyl 2-pyrone (2) may be a useful synthetic precursor of functionalized 2-pyrones[5] because silyl substituents attached to an sp^2 carbon atom are known to be converted into a variety of functional groups.[6] Complete and selective protodesilylations of (2) were carried out and the results are summarized in Scheme 2. Isolated yields of (3) and (4) were 35 and 90%, respectively.

The reaction of ethoxy(dimethylphenylsilyl)ethyne (5) with CO$_2$ gave the new product (7) along with (6) (Scheme 3).§

References

1 D. Walther, *Coord. Chem. Rev.*, 1987, **79**, 135; A. Behr, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 661; P. Braunstein, D. Matt, and D. Nobel, *Chem. Rev.*, 1988, **88**, 747.

2 (a) Y. Inoue, Y. Itoh, H. Kazama, and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3329; (b) D. Walther, H. Schönberg, and J. Sieler, *J. Organomet. Chem.*, 1987, **334**, 377; (c) T. Tsuda, K. Kunisada, N. Nagahama, S. Morikawa, and T. Saegusa, *Synth. Commun.*, 1990, **20**, 313.

3 T. Tsuda, S. Morikawa, R. Sumiya, and T. Saegusa, *J. Org. Chem.*, 1988, **53**, 3140.

4 T. Tsuda, S. Morikawa, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 1989, 9.

5 For 2-pyrone compounds, see, for example: J. Staunton, in 'Comprehensive Organic Chemistry,' vol. 4, ed. P. G. Sammes, Pergamon, Oxford, 1979, p. 629; G. P. Ellis, in 'Comprehensive Heterocyclic Chemistry,' vol. 3, eds. A. J. Boulton and A. McKillop, Pergamon, Oxford, 1984, p. 675; R. K. Dieter and J. R. Fishpaugh, *J. Org. Chem.*, 1983, **48**, 4439; M. E. Jung, J. A. Lowe, M. A. Lyster, M. Node, R. W. Pfluger, and R. W. Brown, *Tetrahedron*, 1984, **40**, 4751.

6 E. W. Colvin, 'Silicon in Organic Synthesis,' Butterworth, London, 1981, ch. 7.

7 P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J. P. Declercq, 'MULTAN 78, A Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data,' University of York, 1978.

8 'XTAL 2.4 User's Manual,' eds. S. R. Hall and J. M. Stewart, Universities of Western Australia and Maryland, 1988.