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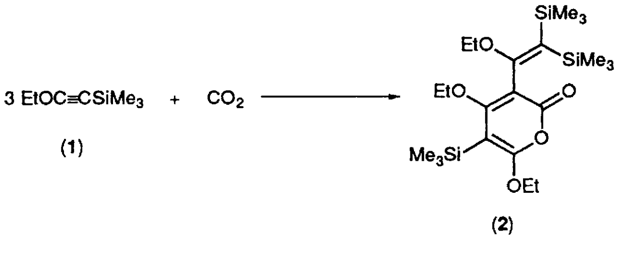
A nickel(0) catalyst, which was generated from bis(cyclo-octadiene)nickel and bis(diphenylphosphino)butane, effected a novel co-oligomerization of three molecules of ethoxy(trimethylsilyl)ethyne with one molecule of carbon dioxide to afford the title compound (**2**) in an excellent yield.

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)-



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

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/cm^2; 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.

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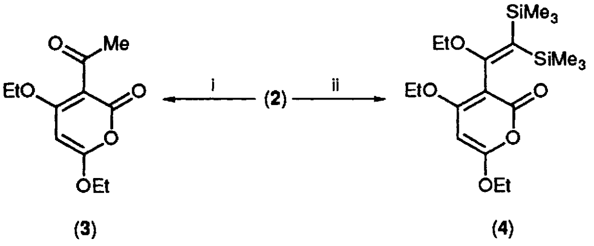
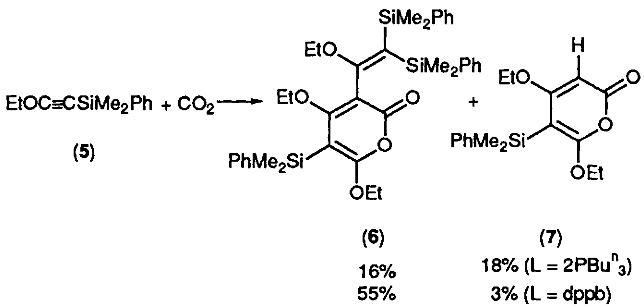
† All new compounds have been fully characterized spectroscopically and their elemental composition has been determined by high-resolution mass spectroscopy.



Scheme 2. *Reagents and conditions*: i, p-$MeC_6H_4SO_2H$, H_2O–MeCN, room temp., 20 h; ii, Bu_4NF, THF, 0 °C, 3 min.



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

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.

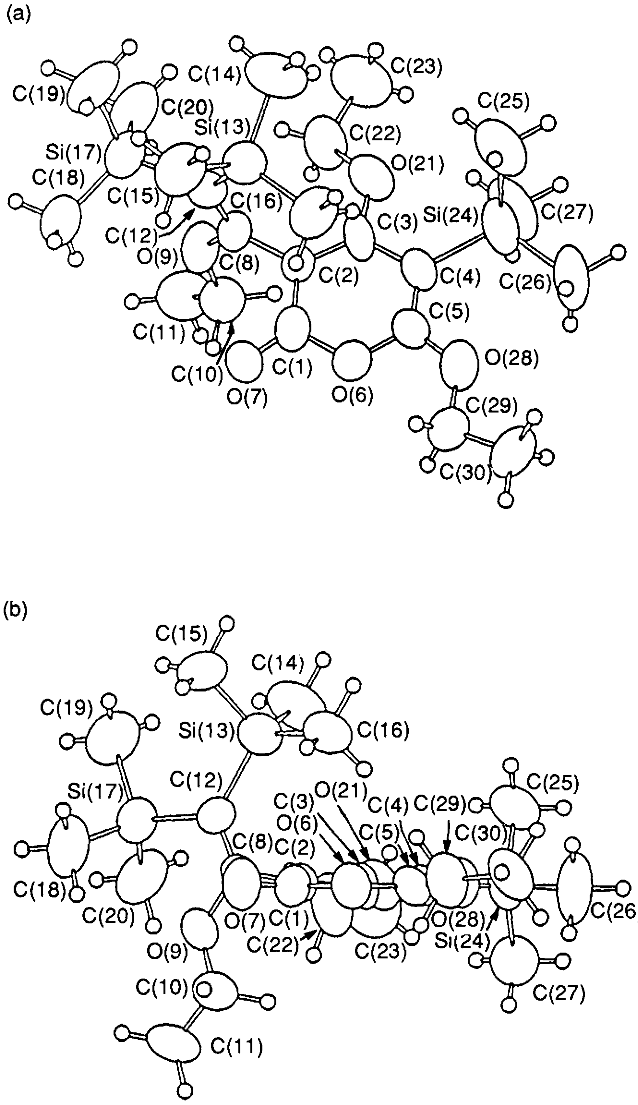


Figure 1. ORTEP drawings of (**2**) from two directions.

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).§

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‡ *Crystal data* for compound (**2**): $C_{22}H_{42}O_5Si_3$, M = 470.91, monoclinic, space group $P2_1/n$, a = 29.003(4), b = 14.623(2), c = 14.453(2) Å, β = 92.16(3)°, U = 6125.5 Å^3, Z = 8, D_c = 1.021 g cm^{-3}, $F(000)$ = 2048, λ(Mo-K_α) = 0.71069 Å, μ = 1.80 cm^{-1}. All measurements were made on a Rigaku AFC-5 diffractometer at room temperature. The crystals were unstable to X-rays and decayed on irradiation. In the data collection reflections were divided into several 2θ-shells including about 1000 reflections, and different crystals were used for individual shells. Reflection intensities were measured by a high-speed scan (8°/min) employing the ω scan mode ($2\theta \leq 31°$) and the ω–2θ scan mode ($2\theta > 31°$), and the background was counted for two seconds at each end. Intensity data were corrected for Lorentz and polarization but not for absorption. Three standard reflections, monitored every 60 measurements, showed a maximum of 14% decrease of F_o values. A total of 6916 independent reflections were measured up to $2\theta = 42°$. All the data sets were scaled and corrected for the decrease based on the F_o values of the standard reflections. The structure was solved by direct methods (MULTAN[7]) and refined by full-matrix least-squares procedures (XTAL[8]) applying anisotropic thermal motion to non-hydrogen atoms. The hydrogen atoms were placed at calculated positions (C–H 1.09 Å) and given an isotropic temperature factor (B = 20.0 Å^2). The final R and R_w values were 0.107 and 0.108, respectively, for 3255 reflections with $F_o > 3\sigma(F_o)$. There were two independent molecules in the asymmetric unit, whose conformations were almost the same. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The source of the C-3 proton of (**7**) is not yet clear; deuterium incorporation at C-3 was not observed using D_2O–DOAc in the work-up, or in co-oligomerization in the presence of D_2O or CD_3CN.

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