

180. Facile Synthesis of Carbon Monoxide Isotopically Labelled at Oxygen from Enriched Water without Isotopic Dilution

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O-Labelled carbon monoxide was prepared on the gram scale from enriched water and acetals of norborn-2-en-7-one (= bicyclo[2.2.1]hept-2-en-7-one) in almost quantitative yields and without isotopic dilution.

^{17}O -NMR has been used in organometallic chemistry for the study of the structure and behaviour in solution of metal carbonyl compounds [1] and is particularly useful for complexes having nuclei with quadrupolar moments, *i.e.* cobalt [2] and manganese [3]. Some metal carbonyls enriched in ^{17}O have been obtained by *Darensbourg* and *Froelich* [4] by phase-transfer reactions using $[\text{Bu}_4\text{N}]\text{OH}/\text{H}_2[^{17}\text{O}]$. A disadvantage of this is that it cannot be used for carbonyl compounds prone to reductive decarboxylation, such as iron carbonyls. Another approach is the direct reaction of enriched carbon monoxide with metal carbonyl compounds using thermal, photochemical, or catalytic means to approach equilibrium concentrations [5]. Labelled carbon monoxide (*ca.* 40% ^{17}O), although commercially available, is very expensive. We report here a simple method for the preparation of $\text{C}[^{17}\text{O}]$ on the liter scale at atmospheric pressure.

The principle of the synthesis is the reaction of a strained acetal with enriched water giving ketones which liberate $\text{C}[^{17}\text{O}]$ upon heating. Since it is known that ketones like bicyclo[2.2.1]hept-2-en-7-one easily decarbonylate [6], the dimethyl acetal of the latter was reacted with $\text{H}_2[^{17}\text{O}]$. The bicyclo[2.2.1]hept-2-en-7- $[^{17}\text{O}]$ one obtained yielded, upon heating, $\text{C}[^{17}\text{O}]$ without isotopic dilution. A similar result was obtained from the dimethyl acetal of tricyclo[3.2.1.0^{2,4}]oct-2-en-8-one.

Experimental. – *Carbon [^{17}O]Monoxide (40% ^{17}O) at 1 bar and Room Temperature from the Bicyclo[2.2.1]heptenone Acetal.* A suspension of 7,7-dimethoxybicyclo[2.2.1]hept-2-ene [7] (7.7 g, 50 mmol) and $\text{H}_2[^{17}\text{O}]$ (40% ^{17}O ; 1.44 g, 80 mmol) acidified by anhyd. H_2SO_4 (50 μl) was stirred for 24 h at 60°. The aq. phase was recovered by decantation and the org. phase distilled at 60°/25 mbar giving bicyclo[2.2.1]hept-2-en-7- $[^{17}\text{O}]$ one (4.0 g, 92%; 40% ^{17}O by MS). A soln. of the $[^{17}\text{O}]$ ketone in dried diglyme (30 ml) was placed in a two-necked flask (50 ml) equipped with a small cooling column (10 cm). The column was connected to a gas buret (1.5 l) through a three-way valve. The system was evacuated and the soln. heated at 145° for 12 h. $\text{C}[^{17}\text{O}]$ (1 l; 40% ^{17}O by MS) was collected and passed through a cooling trap (20 ml, –78°) prior to use.

Carbon [^{17}O]Monoxide from the Tricyclo[3.2.1.0^{2,4}]octenone Acetal. Based on the same principle, a suspension of 8,8-dimethoxytricyclo[3.2.1.0^{2,4}]oct-2-ene [8] (8.3 g, 50 mmol), was acidified (anhyd. H_2SO_4), enriched water (0.8 g, 45 mmol) in dried THF (30 ml) added, and the mixture heated at 50° for 2 h. The $[^{17}\text{O}]$ ketone was not isolated, and $\text{C}[^{17}\text{O}]$ could be directly collected.

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