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# Product Information

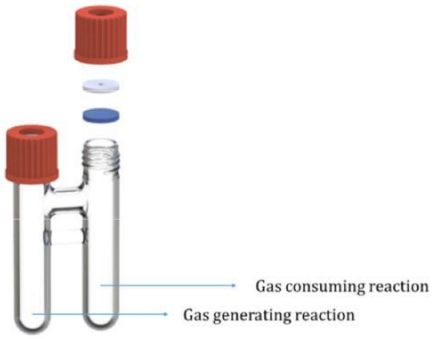
**Gas Generator Kit**
(GasBox)

Product Number **809624**

## TECHNICAL BULLETIN

**Product Description**
The general principle of using the two-chamber glassware (COware) is:

1. The generation of a gaseous reagent in one chamber
2. The simultaneous consumption of the gaseous reagent in the second chamber




Carbon Monoxide (CO) – The use of COware with 9-Methyl-9*H*-fluorene-9-carbonyl chloride (COgen) for generation of carbon monoxide (CO) and carbonylation reactions is detailed in the Procedure section.

The principle of this procedure is applicable for other gaseous reagents. To follow are the gases generated from precursors provided with the Gas Generator Kit.

Carbon Dioxide ($CO_2$) from Sodium Carbonate - Sodium carbonate (1 equiv) and camphorsulfonic acid (2.1 equiv) were added to the carbon dioxide releasing chamber. 1,2 dichlorobenzene (1 mL) was added and finally water (0.7 mL) was added slowly (as a layer on top of the 1,2-dichlorobenzene). The chamber is sealed off using the H-Cap system. Carbon dioxide release is initiated by stirring of the chamber.

Acetylene from 1,1-Diphenyl-2-propyn-1-ol - 1,1-Diphenyl-2-propyn-1-ol (0.5 or 0.75 mmol) was added to the acetylene-generating chamber. Then 1,2-dimethoxyethane (3 mL) and sodium hydride (10 mol %) was added and the chamber was sealed with a screw cap fitted with a PTFE seal. Acetylene release was initiated by heating the chamber to 80 °C.

Ethylene from N,N-Diallyl-4-methylbenzene sulfonamide - N,N-Diallyl-4-methylbenzene sulfonamide (1.2 mmol) was added to the ethylene generating chamber and sealed with a screwcap fitted with a PTFE seal. In a separate flask, Hoveyda-Grubbs 2$^{nd}$ generation catalyst (2.5 mol%) was dissolved in PhMe (2.0 mL) and added to Chamber 2 using a syringe.

Hydrogen ($H_2$) from Granular Zinc and HCl - To one chamber of the COware is added zinc granular and 4 M HCl or DCl. Both chambers are sealed directly after the addition of HCl or DCl, using a screw cap fitted with an H-Cap.

Please refer to the general comments for using COware, found in the Precautions and Disclaimer.

**Components**

| | |
|---|---|
| 9-Methyl-9*H*-fluorene-9-carbonyl chloride (COgen)<br>Product Number 900142 | 5 g |
| N,N-Diallyl-4-methylbenzenesulfonamide<br>Product Number 809632 | 5 g |
| Sodium carbonate<br>Product Number 900143 | 5 g |
| 1,1-Diphenyl-2-propyn-1-ol<br>Product Number 900144 | 5 g |
| Zinc, granular<br>Product Number 900145 | 5 g |
| COware O-rings<br>Product Number 900924 | 40 ea |
| H-Cap system for COware gas reactors<br>Product Number 900925 | 2 ea |
| COware, Product Number 744077 | 1 ea |
| COware PTFE discs, Product Number 743852 | 2 ea |
| COware PTFE/Silicone septa<br>Product Number 743968 | 10 ea |

**Precautions and Disclaimer**
For R&D use only. Not for drug, household, or other uses. Please consult the Safety Data Sheet for information regarding hazards and safe handling practices.

Sigma-Aldrich cannot guarantee glass equipment from breakage under pressure because of varying conditions.

Glass equipment should always be examined for damages to its surface, which may weaken its strength.

One must abide to all laboratory safety procedures and always work behind a shield when working with glass equipment under pressure.

Materials, which solidify upon standing thus causing stress on the glass equipment, should be avoided.

The equipment should not be operated above 60 psi.

The user alone is responsible for calculating the resulting internal pressure when operating COware.

Questions and/or comments can be directed to techserv@sial.com

**Procedure**
Generation of carbon monoxide (CO) from 9-methyl-9*H*-fluorene-9-carbonyl chloride (COgen) using the two-chamber glassware (COware).

1. Remove the red screwcaps from COware including the PTFE-stabilizing discs.
   Note: Prior to use all parts of COware are carefully examined visually for any damages to its surface and the COware should not be used if imperfections are found that would weaken its strength.
2. The COware is placed in a holder on a scale.
3. To one of the two chambers, designated chamber 1, load the following: COgen, $HBF_4P(tBu)_3$ and the palladium-catalyst precursor (i.e. $PdCl_2$, $PdCl_2(COD)$, $Pd(OAc)_2$, $Pd(dba)_2$ etc.) in the amounts required to release the desired amount of carbon monoxide.
   Note: The system should not be operated at pressures higher than 60 psi. The maximum loading of COgen is related to the maximum operating pressure.
   Example for 20 mL COware: With a combined volume of reagents, starting materials, and solvents in the two chambers of 6 mL, a headspace volume of 14 mL results. Loading 2.3 mmol of COgen gives 56 mL CO gas and thus results in a combined internal pressure of 60 psi (70 mL gas in a 14 mL volume) when disregarding heating above ambient temperature, gaseous byproducts, and solvent vapor pressures.
4. To the second chamber, named chamber 2, is loaded the components for the carbon monoxide consuming reaction. Should some of the components be air-sensitive, they should be added after flushing of the COware system (Step 10).
5. COware is removed from the scale and to both chambers are added PTFE coated magnetic stir-bars. Ensure that the stir-bars move freely within the individual chamber to ensure prober stirring during the reaction.
6. The red caps, sealing the COware system, are assembled as follows: The caps are turned upside down. To each cap is inserted one PTFE-Stabilizing disc followed by one PTFE coated silicone seal.

   Note: It is important that it is the white PTFE-surface which faces the glass-chamber of COware. Failing to accomplish this will results in fast deterioration of the PTFE-silicone seal.
7. If oxygen free conditions are required the COware system is assembled by securing the red caps (carrying a PTFE-stabilizing disc and a PTFE coated silicone seal) onto the COware.
   Note: It is important to the performance of the system that the red caps are not tightened too much.

8. The COware system is flushed with argon or nitrogen using a gas inlet and outlet composed of 21G/Ø0.80 mm needles or smaller.
9. Reaction solvents are added to both chambers (suitable solvents in chamber 1 are aprotic solvents such as: THF, Dioxane, Toluene, DME, DMF, DMSO, DMA, PEG, paraffin, anisole, acetonitrile, etc.). Air sensitive reagents can be added to chamber two at this stage, preferably dissolved in the reaction solvent.
10. The trialkyl amine base (triethylamine, *N*,*N*-dicyclohexylamine-*N*-methyl amine, *N*,*N*-diisopropyl-*N*-ethyl amine, or like) is added as the final component to chamber 1. It is important to note that each PTFE coated silicone seal allows for a maximum of two piercings using 21G/Ø0.80 mm needles or smaller. If further piercings are required then the PTFE coated silicone seals should be substituted with new ones while ensuring a positive argon or nitrogen flow on the COware system.
11. Behind a blast shield, the COware system is heated to the desired reaction temperature. The COware system can be operated at temperature ranging from 20–150 °C.
    Notes: Applying standard CO-releasing conditions (Toluene, $HBF_4PtBu_3$, $Pd(dba)_2$, triethylamine, 80 °C) all CO is released within 10 minutes; however, release rate will vary with temperature, solvent, and catalyst loading.
    COware should under no circumstances be operated at pressures higher than 60 psi and/or above the boiling point of the solvent.
12. Upon completion of the reaction the COware system is cooled to room temperature. The crude reaction mixture of chamber two is transferred from the COware system and the contents of chamber one are correctly disposed of.

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