The Quantitative Addition of Air and/or Water Sensitive Compounds to a Hydrogenation Reactor

Introduction

The quantitative hydrogenation of air and/or water sensitive nonvolatile compounds in the presence of organic solvents for indefinitely long periods requires both special reactant transfer methods and a reactor free of parts subject to solvent attack. Two methods of reactant transfer employing all glass systems with fragile bulb break seals in place of stopcocks and grease are described. The first method involves the addition of a solid and the second, the addition of a solution to the reactor 23, Fig. 2. The details cited for these methods, including the manner in which the reactants are initially dispensed into the addition vessels, are determined by the properties of the reactants and the reaction conditions. Such details will vary from case to case. However, the two methods have two principles in common which may be employed to satisfy a wide variety of experimental requirements. These underlying principles are the use of fragile bulb break seals in the inverted or partially inverted position, and the use of gravity to transfer the reactant solution from one volume to another. A measured quantity of hydrogen is added to the reactor at a suitable time.

Experimental Methods

The first method deals with the quantitative addition of a pure, sublimable, hygroscopic solid, for example, $FeCl_3$, to the reaction system. The substance is dehydrated or prepared in the absence of water and if necessary, air and then collected in a vessel sealed onto tube 1 of the solid reactant dispenser, Fig. 1. The system, via tube 3 is pumped down to 10^{-5} Torr and flamed out. The substance is then sublimed into bulb 2. Tubes 1 and 3 are sealed off at the constriction and the solid reactant dispenser is weighed.

The 14/35 standard taper joint 7 is then sealed with black wax into the reactor standard taper joint 7 of Fig. 2. To reduce the possibility of subsequent reactant contamination, black wax is used only on the upper half of the joint. At this time, the vessel 11, containing the solution reactant, is sealed onto the reactor at 14. The reactor 23 is connected to a high vacuum line at 20 using a mercury float valve (1). After the system is pumped down to less than 10^{-5} Torr and flamed out, dry nitrogen is admitted to the reactor 23 and maintained several millimeters above atmospheric pressure during the subsequent operations. Tube 4 is cracked off at a suitable distance from the fragile bulb 5. A rubber policeman containing within it a sharp pointed object, e.g., a hypodermic needle, is then fixed over the open end of 4. The policeman is manipulated so as to break the fragile bulb 5. The policeman is removed and tube 4 is sealed closed at a point removed from the open end so that water does not enter. Just as tube 4 is sealed, the nitrogen flow is discontinued. After a second evacuation and flaming out of the system, the required solvent, stored in the vacuum line, is condensed by a cold bath in the reactor 23. If mercury is to be excluded from the reactor, special precautions may be required (*2*). During all subsequent operations, the black waxed standard taper joint 7 is maintained slightly above room temperature (by a heat gun) so as to avoid solvent condensation and attack. The solvent is warmed to room temperature and a portion of it is condensed onto the reactant in bulb 2 by cooling, for example, with Dry Ice taped to the top of the vessel. The reactant solution is warmed to room temperature and expelled from 2 into 23. By repetition of the cycle, complete transfer is effected. The reactor 23 is then cooled to a temperature at which the solution has negligible vapor pressure and the reactant addition system is sealed off at the

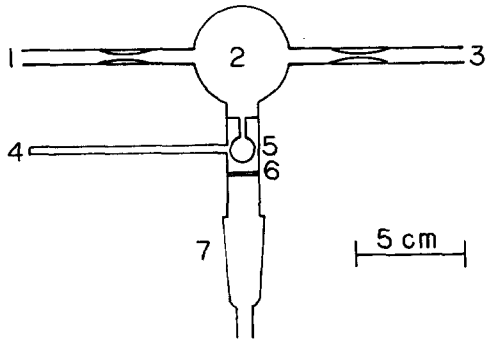

FIG. 1. Solid reactant dispenser.

constriction 21. The empty solid reactant vessel is separated from the standard taper joint, cleaned and reweighed, care being taken to account for all glass fragments from tube 4 and the buoyancy of air.

Presence of the coarse sintered filter at 6 prevents contamination by insoluble components and retention of glass fragments from 5. The diameter of bulb 2 is a function of the reactant quantity. To minimize weighing error, the apparatus should be as small as possible. The distance from bulb 2 to the end of the 14/35 standard taper joint drip tip need not exceed 90 mm. Tube 4 is 4 mm o.d. and tubes 1 and 3, 6 to 8 mm o.d. The total vessel weight (empty) is 20 to 30 g.

The second method deals with the addition of an air and/or water sensitive solution to another in the presence of hydrogen which is absorbed for a period beginning with solution mixing and extending for several months. The liquid reactant addition bulb 11, Fig. 2, containing the solution, is sealed onto the reactor at 14 as indicated previously. After solution transfer of the first reactant to 23 and admission of a known quantity of hydrogen via the fragile bulb break seal 15, the reactant in 11 is introduced by breaking the fragile bulb 13 with a Teflon (DuPont) coated magnet 12. When not in use, 12 is arrested by an externally taped bar magnet. It may be necessary to force this reactant into 23 by slightly heating

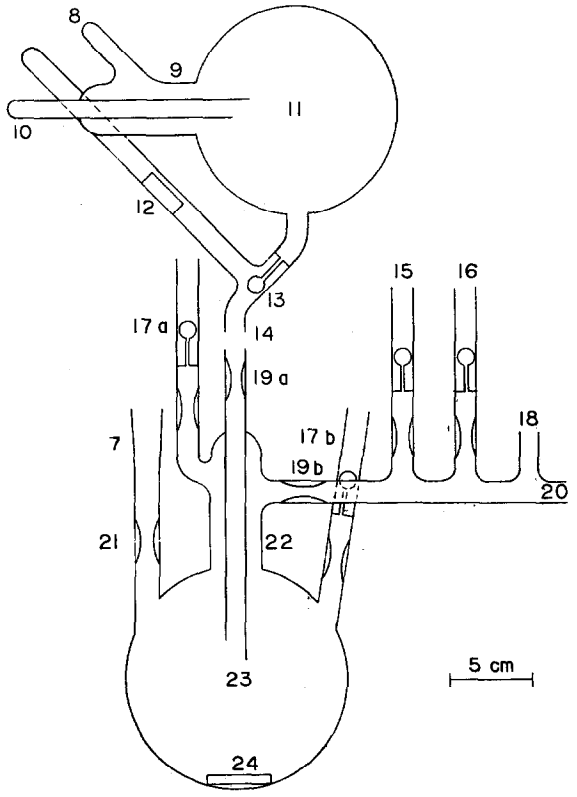

FIG. 2. Reactor and solution reactant dispenser.

and/or cooling 11 and/or 23. A Toricelli type manometer, previously sealed on at 18, is used to follow the pressure change. The solution is magnetically stirred with the Teflon (DuPont) coated bar magnet 24. When reaction ceases, as indicated by no further pressure decrease, the excess hydrogen is determined by passage through a trap cooled to −196°C, and then forced into a calibrated volume by a Toepler pump. Subsequently, volatile, condensable products are transferred to a vacuum line and separated by conventional means, for example, distillation and fractional condensation. Access to the volatile products is via fragile bulb 16. Manipulation of the nonvolatile products, for example filtration, is accomplished by first sealing off the constrictions 19a and 19b and then by access through fragile bulb 17a or 17b. The thickened portion at the base of each break seal permits separation of the reactor for subsequent operations. It is good practice to seal closed the exposed end of the fragile bulb break seals in the manner cited in Ref. (*3*).

Apparatus dimensions are determined by the particular experiment. Most connecting tubing, particularly those parts that are later sealed off, does not exceed 12 mm o.d. Clamping of the apparatus shown here to a fixed lattice should employ no more than two 3-finger clamps, one at 9 and one at 22. Overclamping of any vacuum apparatus is to be avoided for there is less chance to relieve strain and consequently greater chance for failure.

The two techniques cited were developed for the study of the reaction of an ethereal solution of $FeCl_3$ with phenyl Grignard under an atmosphere of hydrogen (*4*). The $FeCl_3$ was prepared from the anhydrous elements in an all glass evacuable system. Purification was accomplished by vacuum sublimation of the $FeCl_3$ into the solid reactant dispenser, Fig. 1. The only contaminant present was a slight amount of the ether-insoluble $FeCl_2$. The Grignard was prepared under an atmosphere of dry nitrogen and filtered into the solution addition vessel 11. Hydrogen, stored in a 5-liter calibrated bulb provided with a Toricelli type manometer, was introduced into the reactor via fragile bulb 15. An additional fragile bulb break seal should be provided for entry into the reactor system for eventualities not contemplated beforehand. For example, a second fragile bulb break seal was required for introduction of an additional 5 liters of hydrogen.

The manner of Grignard transfer into bulb 11 warrants an explanation. Bulb 11 originally possesses a ball joint beyond point 10 and a three way stopcock beyond point 8. The stopcock is used to either evacuate the vessel or to admit dry nitrogen. After formation of the Grignard in a flask equipped with 24/40 standard taper joints, the ethereal solution is forced by a positive nitrogen pressure into an all glass filter-delivery tube which is connected to bulb 11 via tube 10. The filter-delivery tube, shaped in the form of an inverted letter U, is equipped with a 24/40 joint at one end, a socket joint at the other, and a medium sintered filter. When filtration is complete, the ball joint at the end of tube 10 is capped. After cooling the solution to −80°C, the bulb is evacuated and then the solution is warmed to room temperature. By a condensation process, the interior of tube 10 is washed free of solvent. The solution is again cooled and tubes 10 and 8 are sealed off. While the Grignard was not assayed in this experiment, the apparatus could be designed to permit withdrawal of a measured aliquot from a solution whose volume was also measured.

References

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