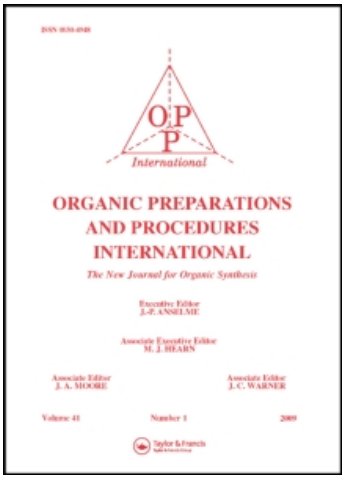

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A HIGH-DILUTION APPARATUS FOR THERMALLY UNSTABLE REACTANTS

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To cite this Article Frcaşiu, D.(1973) 'A HIGH-DILUTION APPARATUS FOR THERMALLY UNSTABLE REACTANTS', Organic Preparations and Procedures International, 5: 3, 113 — 116
To link to this Article: DOI: 10.1080/00304947309355557
URL: http://dx.doi.org/10.1080/00304947309355557

ORGANIC PREPARATIONS AND PROCEDURES INT. 5(3), 113-116 (1973)

A HIGH-DILUTION APPARATUS FOR THERMALLY UNSTABLE REACTANTS

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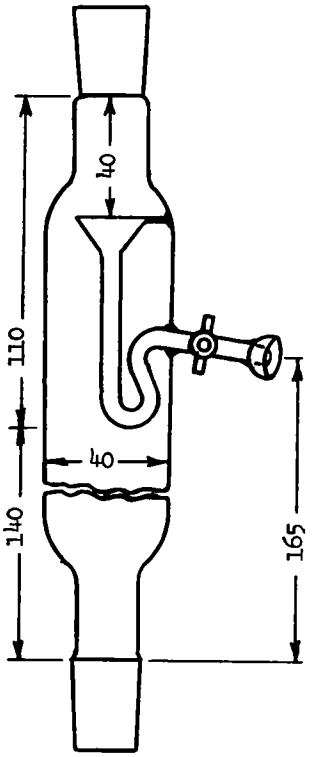
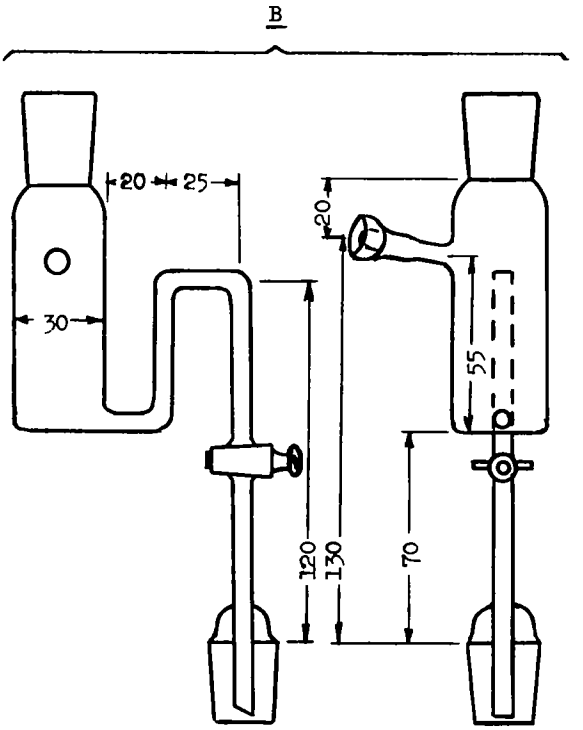
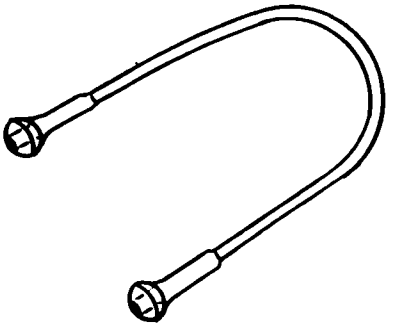
High-dilution technique is used to favor an intramolecular reaction over the competing intermolecular one, which would prevail at higher concentration of reactants. The total volume is kept to practical limits by using an apparatus designed to allow refluxing solvent to dilute the reactants. However, in the assemblies described for this purpose,[1,2] the reactant being diluted comes in contact with hot solvent vapors and heated parts of the installation before being dispersed into the reacting mixture. Such designs are unsuitable for heat-sensitive compounds.

We have devised a simple high-dilution apparatus in which a thermally unstable compound can be added while cool to the refluxing solution of the other reagent (or catalyst) with negligible prior contact with hot vapors or heated parts of the apparatus. The apparatus sketched in the Figure consists of three parts: the collector of refluxing solvent made of glass (A), the mixing chamber (B) also made of glass, and the metal tube (C)[3] (3 mm O.D., 1 mm I.D., 350 mm long) welded to Kovar/Pyrex seals which end with spherical joints No. 18/9 (the dimensions in the figure are given in mm). Parts A and B are mounted on the outer necks of a three-necked flask[4] and are connected by tube C. The assembly, viewed from above, is shown in D. Tube C is kept in place with semi-ball type clamps.

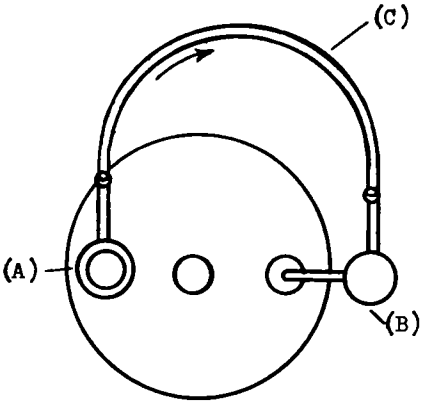


A





C



D

A reflux condenser is placed at the top of A, and the heat-sensitive reactant is added from the dropping funnel attached to B. Although the tube C could also be constructed from glass, we found metal to have definite advantages.[3] A copper tube has excellent heat transfer properties. The solvent collected in A enters B at, or slightly above, room temperature. For even better cooling, air may be blown on tube C or it can be sprayed with cold water. In addition, the flexibility of the metal diminishes the risk of breaking and allows the use of the assembly on flasks of various sizes. The mixing chamber B can be kept in a cooling bath and its content can be magnetically stirred. The syphon at the bottom of B ensures a good flow through the narrow tube (C) and complete drainage of B. The dilution ratio can be adjusted in various ways, e.g., by varying the dropping rate of reactant into B and of solution from B into the reaction flask. The stopcock in A[5] allows total reflux by shutting off completely parts B and C.

The apparatus was employed for the synthesis of five-membered ring ketones by copper salt catalyzed decomposition of diazoketones.[6] In one case, the yield of cyclized product was increased from 10% to 55% using this high-dilution assembly, while the intermolecular reaction (dimerization of the ketocarbene) was reduced from 42% to 1-2%.

Acknowledgments. This work was funded by grants from the National Institutes of Health (GM 19134), the National Science Foundation (GP-29078X), the Petroleum Research Fund, administered by the American Chemical Society, and Hoffmann La Roche, Inc., Nutley, N. J. Support and encouragement by Professor P. von R. Schleyer is gratefully acknowledged. Messrs. H. Olson and L. Lloyd aided in the construction of the apparatus.

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4. R. Adams and N. Kornblum, J. Am. Chem. Soc., 63, 188 (1941).

5. Teflon stopcocks are used in the apparatus.

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(Received April 25, 1973; in revised form June 14, 1973)