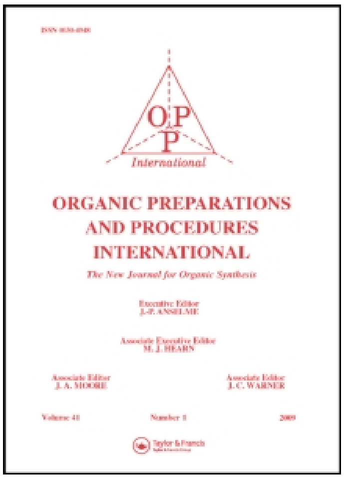

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A VARIABLE TEMPERATURE PREPARATIVE SCALE PHOTOCHEMICAL REACTOR.

CIS-DIMETHYL BICYCLO[3.2.0]HEPTANE-1,5-DICARBOXYLATE

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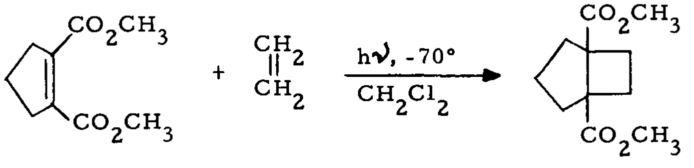
The use of low temperatures to carry out a variety of photochemical transformations has been shown to offer a number of advantages. Among these are higher quantum yields, fewer undesirable side products and greater solubility of gaseous reactants.[1] However, it is often difficult to carry out such transformations on a preparative scale at low temperatures. The intense heat of the 200 or 450 watt mercury arcs commonly in use for preparative work presents major problems in cooling a solution which is in contact with an immersion well containing the hot lamp. Furthermore, the use of water to cool the lamp presents the additional danger of cracking an expensive lamp housing and also ruining a lamp should the water suddenly freeze.[2]



(1)

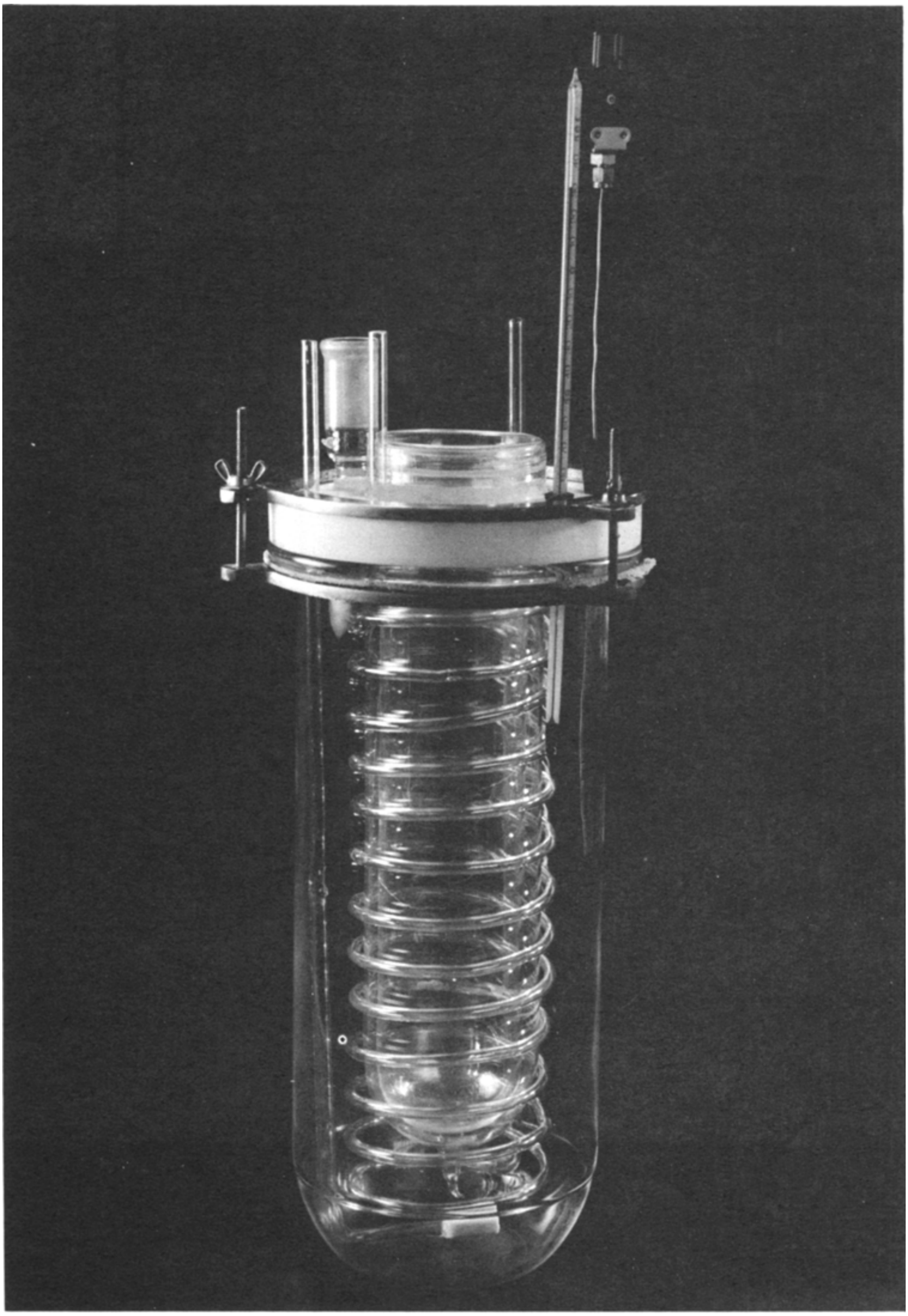
1

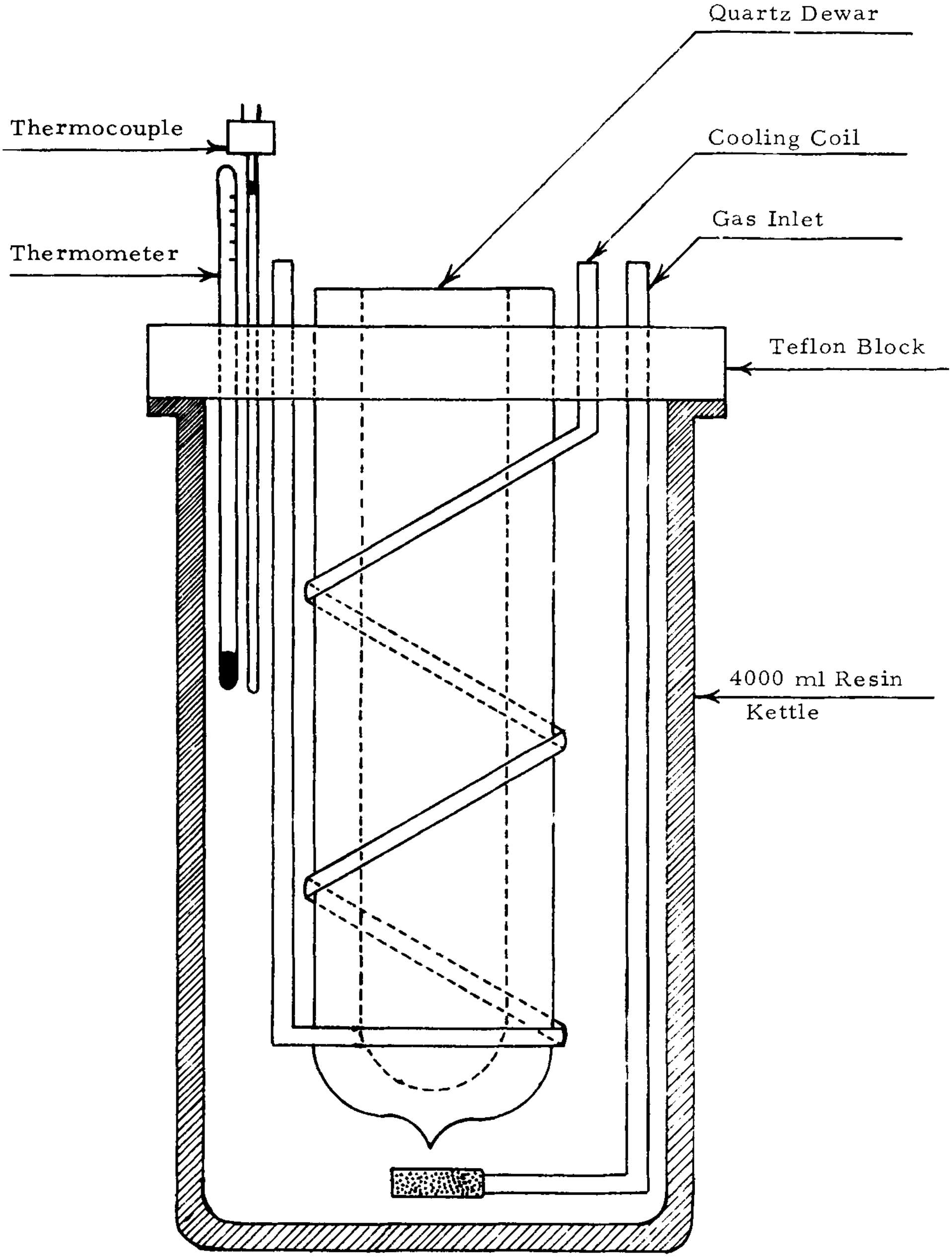
2, 89%

We have designed and built a relatively inexpensive variable temperature preparative scale photochemical reactor which overcomes much of the difficulty discussed above. The photochemical [2+2] cycloaddition of ethylene to dimethylcyclopentene-1,2-dicarboxylate, **1**, is offered as an example of the use of the reactor at low temperatures (eq. 1). The yield of analytically pure cis-dimethyl bicyclo[3.2.0]heptane-1, 5-dicarboxylate[3] is 89%.

The photochemical [2+2] cycloadditions of ethylene to electronically excited conjugated olefins have not received very much attention.[4-8] In light of the great amount of work on substituted ethylenes,[2, 9-12] this may be due either to low quantum efficiencies of the ethylene reactions or to decreased solubility of ethylene at or near room temperature. For example, when a solution of 92g of **1** in ethylene saturated methylene chloride was irradiated at 10° for 6 days, only 40% of starting material was consumed. After the solution was cooled to -70° in the variable temperature reactor, the photolysis was completed in only 18 hours. We have used this reactor to carry out [2+2] cycloadditions of ethylene and acetylene to a variety of carbonyl conjugated olefins with very high preparative yields and quantum efficiencies.[13]

The central core of the reactor is a transparent quartz Dewar which serves to isolate the lamp and lamp housing from the cold solution. A photograph and schematic drawing of the apparatus is shown on the following pages. The use of the Dewar to isolate the lamp housing from the solution offers two distinct advantages: (1) a low rate of heat transfer from the lamp to the solution, and (2) cooling of the lamp by ordinary





Variable Temperature Photochemical Reactor tap water without fear of breaking the lamp housing. Furthermore, a thermostatted cooling system allows the temperature of the solution to be automatically controlled from -100° to room temperature. The reactor also offers precise, automatic control of the solution temperature at or above room temperature because of the isolation of the lamp housing from the solution. We have carried out a variety of preparative scale photolyses at temperatures ranging from -80° to +80° with a great deal of success.

EXPERIMENTAL

Reactor Design. Although the reactor can be built in any convenient size, we shall describe the dimensions of a reactor which contains 2800 ml of solution and accomodates a Hanovia lamp housing with a 55/50 standard taper joint. The Dewar has the following dimensions: inside: 62 mm diameter x 320 mm deep; outside: 81 mm diameter x 340 mm deep. It is made entirely of quartz (evacuated to 10^{-5} torr at 100°) and is seated in a Teflon* block (19 mm thick and 175 mm in diameter) which rests on the top of a 4000 ml resin kettle. Holes are drilled into the block to accomodate an 8 mm O.D. Pyrex cooling coil, a fritted gas dispersion tube that reaches to the bottom of the reactor, a 10/30 standard taper thermometer and a 19/22 standard taper joint for a condenser or dropping funnel. Small holes are also drilled for a stainless steel-jacketed iron-constantan thermocouple and a serum cap for sampling.

Cooling System. Cold nitrogen pumped from a 50-ℓ liquid nitrogen

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reservoir is the principal coolant for the reactor. The nitrogen is passed through the reactor cooling coils by applying pressure to the reservoir from a nitrogen source. The rate of coolant flow is controlled by an Asco #831735 3-way solenoid valve which is activated by a Sim-Ply-Trol Pyrometer connected to the thermocouple in the solution. The same thermocouple and controller is used for both high and low temperature work by a simple reversal of the thermocouple leads and recalibration of the pyrometer scale. A secondary cooling system is provided by immersing the reactor in a Dry Ice-acetone bath in an insulated bucket. By using the dual coolant system the liquid nitrogen supply needs to be replenished only every 24-27 hours and the Dry Ice only every 6-8 hours to maintain a temperature of -80° while photolyzing with an Hanovia 450 watt medium pressure mercury arc. If a multistage refrigerated cooling system is available, the reactor configuration can be easily adapted to the use of a thermoregulated pump to circulate coolant through the coils in order to maintain even more precise temperature control.

Materials. Dichloromethane (Matheson, Coleman and Bell) tetrahydrofuran (THF) (Fisher), methanol (Mallinckrodt) and ethylene (Matheson, C. P. grade) were used without further purification. Thionyl chloride (Fisher) and bromine (Mallinckrodt) were used directly from the bottle. Pimelic acid was recrystallized from water.

Dimethyl cyclopentene-1,2-dicarboxylate. A slurry of 109.7 g (0.68 mol) of pimelic acid and 200 g (1.68 mol) of thionyl chloride was prepared in a 1-ℓ round bottomed flask equipped with reflux condenser and nitrogen bubbler. The mixture was magnetically stirred and heated with an oil bath for 3 hr. The excess thionyl chloride was drawn off in vacuo and then 250 g (1.56 mol) of bromine was added to the crude acid chloride over 4 hr. from an addition funnel while the solution was irradiated with a 150 watt incandescent bulb. A temperature of 80° was maintained during the addition. The reaction then was heated and irradiated for an additional 4 hr. The red mixture was transferred to an addition funnel and added over 15 min. to 500 ml of methanol chilled to 0°. The methanolic solution was poured into 500 ml of water. The lower layer was separated and the top aqueous layer was extracted with 1000 ml of ether. The ether extract was combined with the lower layer and the entire solution was washed once with 500 ml of a 10% sodium metabisulfite solution, twice with 500 ml of a 3% sodium carbonate solution and once with 100 ml of water. The extracts were dried over anhydrous potassium carbonate and concentrated in vacuo to give 234.3 g of a light yellow oil.

The crude dimethyl-α,α'-dibromopimelate was added to a slurry of 54.4 g (1.3 mol) of a 56.6% sodium hydride dispersion and 1 ml of tert-butyl alcohol in 2500 ml of THF in a 5-ℓ round bottomed flask under nitrogen. The solution was stirred for 18 hr. and refluxed for 4 hr. Acetic acid was added (5 ml) and the solution was filtered and concentrated. The resulting oil was taken up in 300 ml of water and extracted twice with 200 ml portions of petroleum ether and once with ether. The extracts were dried over magnesium sulfate and concentrated in vacuo. The resulting oil was distilled at 66-68°/0.11 mm (lit[14] 120-5°/11 mm) to yield 85.4 g (0.46 mol, 67.7%) of dimethyl cyclopentene-1,2-dicarboxylate, n_D^{25} 1.4736.

Dimethyl bicyclo[3.2.0]heptane-1,5-dicarboxylate. A solution of 27.6 g (0.15 mol) of dimethyl cyclopentene-1,2-dicarboxylate was prepared in 2800 ml of dichloromethane and cooled to -70° in the variable temperature reactor. The solution was flushed with nitrogen for 15 min. and then ethylene was bubbled through it at a flow rate of 100 ml/min for 1 hr. The solution was then subjected to direct irradiation from a 450 watt Hanovia medium pressure mercury arc for 3 hr at -70°. An ethylene flow rate of 50 ml/min was maintained during the irradiation. The solution was allowed to warm to room temperature under nitrogen and was then concentrated *in vacuo*, to yield 30.6 g (96%) of crude product. Distillation of this oil at 75.5-76°/0.2 mm gave 28.2 g (0.138 mol, 89%) of analytically pure *cis*-dimethyl bicyclo[3.2.0]heptane-1,5-dicarboxylate.[3] *Anal.* Calc'd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found C, 62.04; H, 7.75. Nmr (CCl_4 solvent, TMS reference) 3.58 δ (singlet -6H) 2.57 δ (complex multiplet -6H) and 1.6 δ (complex multiplet-4H). n_D^{25} 1.4691.

In another experiment, 92.0 g (0.5 mol) of dimethyl cyclopentene-1,2-dicarboxylate was irradiated for 6 days at 10° in 4500 ml of dichloromethane which had ethylene flowing through it. Glc examination showed that only 40% of the starting ester had been consumed in this time. After the solution was concentrated to a volume of 2800 ml, it was irradiated as described above at -70° in the variable temperature reactor for 18 hr. Glc examination showed that the remaining 60% of starting ester had been consumed in this time. A yield of 80.4 g

(0.38 mol, 76%) of bicyclic product was obtained.

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