$[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]$decane (314 mg, 2 mmol) in 3 mL of dry THF at −78 °C. Dry oxygen was bubbled at a moderate rate into the lithionitrile solution for 60 min at −78 °C. The reaction was quenched with 10 mL of 1 M stannous chloride in 2 M HCl and stirred for 2 h at ice temperature. The reaction mixture was diluted with water (30 mL) and extracted with ether (2 × 25 mL). Washing of the ether extract with 1 M NaOH and concentration yielded an oily residue. Direct bulb-to-bulb distillation up to 100 °C (1.5 mm) yielded 148 mg (51%) of **2** as an oil and a small uncharacterized solid residue remained. The ketone solidified on refrigeration and could be crystallized from petroleum ether as a low-melting solid: IR (neat)[13] 3045, 1725, 1675, 795, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.5–2.9 (m, 2 H), 1.9–2.3 (m, 4 H), 1.4–1.9 (m, 4 H).

Sodium borohydride reduction of **2** furnished pentacyclo$[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]$decan-9-ol, mp 126–128 °C (lit.[1] mp 129 °C).

1,4-Dibromopentacyclo$[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]$nonan-9-one Ethylene Ketal (9). To a boiling solution of 1-bromo-9-oxopentacyclo$[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]$nonane-4-carboxylic acid ethylene ketal[9] (**8**) (2.07 g, 6.7 mmol) in methylene bromide (15 mL) containing suspended HgO (1.7 g, 7.4 mmol) was added dropwise a solution of bromine (1.7 g, 10.6 mmol) in CH_2Br_2 (2 mL) with magnetic stirring. The mixture was heated under reflux for 4 h. The methylene bromide was removed under reduced pressure and the residue was extracted with hot hexane. Removal of hexane furnished 1,4-dibromohomocubanone ketal (**9**) (2.01 g, 90%) as a white solid: mp 141 °C (lit.[14] mp 143–144 °C); IR (KBr) 3020, 1290, 1075 cm^{-1}.

Pentacyclo$[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]$nonan-9-one (3). To a solution of 1,4-dibromohomocubanone ketal (**9**) (1.5 g, 4.5 mmol) in dry THF (30 mL) and *t*-BuOH (1.5 mL) was added lithium metal (0.5 g, 0.071 mmol) and the mixture was heated at reflux temperature for 1 h. The excess lithium was destroyed by carefully adding water (20 mL) and the aqueous solution was extracted with CH_2Cl_2. Evaporation of the CH_2Cl_2 furnished a yellow oil (0.71 g, 94%); IR (neat) 3000, 2900, 1325, 1200, 1100 cm^{-1}. A suspension of the above yellow oil in 5% aqueous H_2SO_4 was stirred vigorously at room temperature for 15 h. The reaction mixture was extracted with ether and the ether extract was washed with 5% aqueous $NaHCO_3$ and water until neutral. Removal of solvent at low temperature furnished homocubanone (0.5 g, 90%). Crystallization from petroleum ether furnished white crystals: mp 66–67 °C (lit.[2] mp, 66–68 °C); IR (CCl_4) 3000, 1770, 1710, 1240, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.63 (m, 6 H), 2.99 (m, 2 H); mass spectrum, m/e 132.0575 (M^+, C_9H_8O).

1,4-Dideuteriopentacyclo$[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]$nonan-9-one (10). To a mixture of 1,4-dibromohomocubanone ketal (**9**) (4.0 g, 12 mmol) in dry THF (60 mL) and *t*-BuOD (2.213 g) was added fine pieces of lithium metal (0.9 g, 0.129 mol) and the reaction mixture was heated at reflux temperature for 3–4 h. The excess lithium was destroyed by carefully adding water (20 mL) and the aqueous mixture was extracted with methylene chloride. Removal of solvent furnished a yellowish oil (1.9 g, 90%); IR (neat) 2980, 2890, 2250, 2240, 1305, 1205, 1190, 1100, 1060 cm^{-1}.

The above oil was suspended in 5% aqueous H_2SO_4 and stirred at room temperature for 15 h. The aqueous solution was extracted with CH_2Cl_2 and the organic layer was washed with 5% aqueous $NaHCO_3$ and water until neutral. Removal of methylene chloride at low temperature furnished 1,4-dideuteriohomocubanone (**10**) (1.30 g, 90%). Crystallization from petroleum ether furnished white crystals: mp 67 °C; IR (CCl_4) 3000, 2270, 2245, 1770, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.63 (m, ~5 H), 3.00 (m, ~1 H); mass spectrum, m/e 134.0698 (M^+, $C_6H_6d_2O$, $d_2 = 49\%$, $d_1 = 35\%$, $d_0 = 16\%$).

Acknowledgment. We acknowledge the support of this research by SERC, Department of Science and Technology, Government of India.

Registry No. **1**, 10555-62-1; **2**, 75299-35-3; **3**, 15291-18-6; **4**, 5603-27-0; **5**, 73395-57-0; **6**, 75311-37-4; **7**, 75299-36-4; **8**, 25867-86-1; **9**, 37794-26-6; **10**, 75299-37-5.

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An Improved Apparatus for the Laboratory Preparation of Diazomethane

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Received July 29, 1980

The laboratory preparation of diazomethane from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) as described in *Organic Syntheses* (1963)[1] suffers from some minor disadvantages. The main of them is the difficulty of condensing all the diazomethane and ether vapors. Even if two consecutive ice-cooled receivers of the diazomethane solution are used as described in the procedure[1] some of the product escapes unless the distillation is carried out very slowly and the cooling water is colder than about 10 °C. This flaw can be partly removed by using chilled water (8 °C) in an apparatus suitable for a large-scale preparation of diazomethane.[2] However, such an arrangement often requires a circulation pump.

A simple compact apparatus shown in Figure 1 makes possible a quantitative collection of an ether solution of diazomethane prepared from the same starting materials as described in the published procedures.[1,2] The crucial part of the apparatus is a specially adapted *dry ice reflux condenser.*

The apparatus consists of a three-necked round-bottomed flask (250–1000 mL) immersed in a water bath and equipped with a Teflon-coated magnetic stirring bar, a thermometer, a separatory funnel (100–500 mL) with a pressure equalizer, and a *special dry ice reflux condenser* (A). This is fitted with a Teflon stopcock (B) and an overflow trap (C), a ground-glass joint (D) connected to a receiver of the diazomethane–ether solution, and an outlet (E) which is connected to a dry ice trap.

Experimental Section

Procedure. The three-necked flask (500 mL) is charged with a solution of 18 g (0.32 mol) of potassium hydroxide in 30 mL of water, 105 mL of Carbitol (diethylene glycol monoethyl ether), and 30 mL of ether. The pocket of the special condenser (A) is filled with dry ice and acetone, and the separatory funnel (500 mL) with a solution of 64.2 g (0.3 mol) of Diazald in 375 mL of ether. A 500-mL Erlenmeyer flask immersed in ice–water is connected to the ground-glass joint (D) of the condenser. The water bath is heated to 60 °C, the magnetic stirring is started, and the solution of the Diazald is introduced at such a rate that all the yellow vapors evolved are completely condensed in the reflux condenser with the stopcock (B) closed. Then the stopcock is opened. The first portions of the yellow condensate fill the overflow trap (C) which allows the liquid to flow into the receiver but prevents the undesirable passage of uncondensed vapors past the receiver. The temperature of the water bath is gradually raised to 70–80 °C until all the Diazald solution is used up and the condensate in the dry ice condenser is colorless (ether).

With proper replenishing of the dry ice in the condenser (A) (about 2 kg are needed for 0.3 mol of diazomethane), a practically quantitative recovery of diazomethane and ether is achieved within 90–100 min. Four hundred milliliters of the ethereal solution is collected, containing, according to the titration with ethereal benzoic acid, up to 0.27 mol of diazomethane (90% yield).

The apparatus and the procedure were tested by several runs ranging from 0.2 to 0.3 mol of Diazald and were found both efficient and safe. The few flame-polished ground-glass joints (well greased with a stopcock grease) are stationary and are not

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(2) P. H. Ruehle, C. E. Browne, and E. J. Eisenbaum, *Chem. Ind.* (*London*), 225, (1979).

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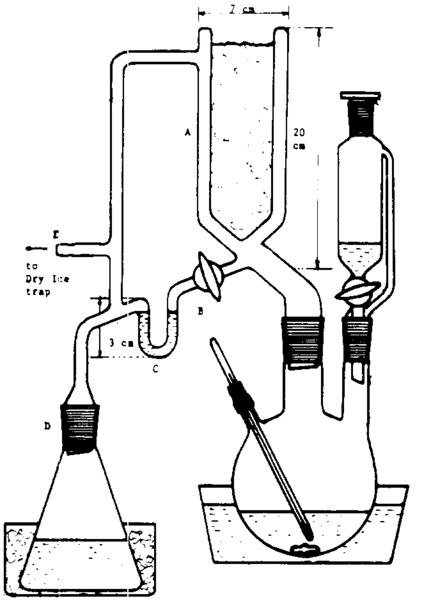

Figure 1.

moved during the whole operation, the only mobile parts being the Teflon-coated stirring bar and two Teflon stopcocks. The apparatus is disassembled only when all the diazomethane solution has distilled off.

Just to be on the safe side, all other precautions necessary for the work with diazomethane[1,2] such as working in a hood with the hood door of shatter-proof glass, etc.[1,2] were strictly observed.

Registry No. Diazomethane, 334-88-3.

Synthesis of the C_{2v}- and S_4-Symmetric Tetraesters of Tricyclo[3.3.0.0^{3,7}]octane

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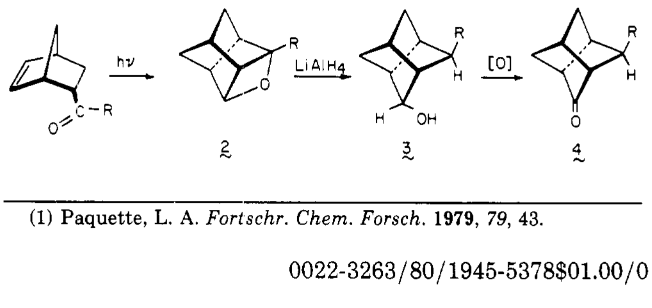
Received August 15, 1980

The tricyclo[3.3.0.0^{3,7}]octane ring system (1) brings to

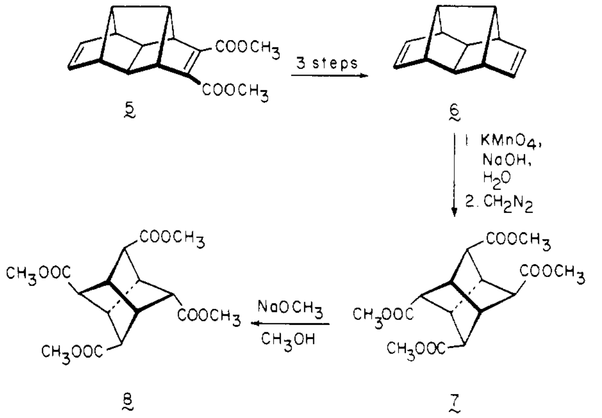
1

the polyquinane field[1] the same degree of fascination which tetrahedrane, cubane, and adamantane offer to the alicyclic chemistry of polycondensed three-, four-, and six-membered rings, respectively. Despite the highly symmetrical arrangement of the fused cyclopentane rings within 1, its properties have not been widely exploited. Sauers and co-workers have developed an apparently general approach to tricyclo[3.3.0.0^{3,7}]octan-2-ols (3) which consists of the Paterno–Büchi photocyclization of *endo*-5-acylnorbornenes followed by reductive cleavage of the resultant oxetanes 2.[2] Oxidation of 3 affords the ketones 4 to which Windhorst has assigned the trivial name "natones" to emphasize the relationship of their four-pointed-star appearance to the NATO symbol.[3] Although other syntheses of this ring system are known,[4] none have provided access to derivatives having more than one functional group at the secondary sites. It has already been made clear that care must be exercised in handling certain monosubstituted tricyclo[3.3.0.0^{3,7}]octanes since they are particularly prone to rearrangement.[2c,4d,5]



In this note, we detail a convenient synthesis of two highly symmetric tetracarboxylate esters of 1 and make mention of certain observations which relate to the sensitivity of these molecules.

Our strategy centered around the diene 6 which we have earlier shown to be available by three-step chemical manipulation[6] of 5, a domino Diels–Alder adduct of 9,10-dihydrofulvalene and dimethyl acetylenedicarboxylate.[7] This diene possesses, in somewhat masked form, the complete tricyclo[3.3.0.0^{3,7}]octane framework (note the cross-hatched arrangement of upper and lower bonds in the central region of the molecule) and a pendant carbon atom at each of the five-membered rings. Ozonolysis of 6 under a variety of conditions followed by oxidative workup (H_2O_2, MCPBA, etc.) led invariably to a mixture of difficulty separable materials, esterification of which provided no detectable amounts of the desired tetraester 7. The ^{1}H NMR spectra of the residues indicated clearly that no 6 remained and suggested that skeletally rearranged materials had been produced (no evidence of symmetry). Previously, we had demonstrated that the perhydromethenocyclopenta[*a*]pentalene framework which 6 possesses is particularly susceptible to cationic Wagner–Meerwein shift.[8] Conceivably, therefore, electrophilic attack by ozone at the double bonds in 6 is accompanied by framework isomerization. Whatever the difficulty, the problem persisted when 6 was treated with potassium permanganate in dry acetone at room or reflux temperature for varying amounts of time.[9]



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