the absence of a suitable trapping agent, decomposes to water-soluble products.[5]

The sulfonylamine mechanism which is used extensively in the above discussion is supported by the observation that the *N,N*-diethylsulfamate ester **3**, which lacks the acidic N-H required for base-promoted elimination, is inert to benzylamine in refluxing dioxane (16 h of reflux). This is in good agreement with observations made earlier on the reaction of **3** with inorganic bases.[1]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Proton magentic resonance spectra were recorded on a Varian Associates T-60A spectrometer (60 MHz) and are recorded in parts per million from tetramethylsilane. Elemental analyses were carried out by the Stanford University Microanalytical Laboratory. Melting points were determined on a Thomas-Hoover melting-point apparatus and are uncorrected. Thin-layer chromatography (TLC) was carried out on EM Laboratories precoated silica gel 60 F-254 plates (5 × 10 cm). Solvents and reagents used were reagent grade as obtained from either J. T. Baker or Aldrich Chemical Co., except for dioxane which was distilled from $LiAlH_4$ and stored over activated molecular sieves (4 Å).

General Procedure for Amination of 2-Hydroxyphenyl *N*-Benzylsulfamate (1). Dry dioxane (5 mL) was added to a mixture of 279 mg (1.00 mmol) of **1** and 1.10 mmol of amine after which the resultant solution was refluxed under dry argon until TLC ($CHCl_3/CH_3OH$, 93:2) indicated that all **1** (R_f 0.17) had been consumed. The reaction mixture was then allowed to cool and poured into 50 mL of 5% HCl. The precipitated sulfamide was then suction filtered and recrystallized from absolute EtOH.

***N,N'*-Dibenzylsulfamide (10).** According to the general procedure, 118 mg (1.10 mmol) of benzylamine was reacted with 1.00 mmol of **1** for 2 h to give 252 mg (91%) of **10** as colorless plates: mp 180–182 °C (lit.[3e] mp 181–182 °C); TLC R_f 0.27; IR (KBr) 3.02 (NH), 7.64 (S=O), 8.75 (S=O) μm; NMR (acetone-d_6) δ 4.17 (br s, 4 H, $PhCH_2N$), 7.00 (br s, 2 H, NH), 7.37 (s, 10 H, Ph H). Anal. ($C_{14}H_{16}N_2O_2S$) C, H.

***N*-Benzyl-*N'*-cyclohexylsulfamide (11).** According to the general procedure, 109 mg (1.10 mmol) of cyclohexylamine was reacted with 1.00 mmol of **1** for 2.5 h to give 241 mg (90%) of **11** as colorless plates: mp 133–135 °C; TLC R_f 0.28; IR (KBr) 3.03 (N-H), 7.61 (S=O), 8.75 (S=O) μm; NMR ($CDCl_3$) δ 0.83–2.25 (m, 10 H, $(CH_2)_5$), 3.20 (m, 1 H, NCH), 4.08–4.90 (br s, 2 H, NH), 4.18 (d, 2 H, J = 6 Hz, $PhCH_2N$), 7.33 (s, 5 H, Ph H). Anal. ($C_{13}H_{20}N_2O_2S$) C, H.

***N*-Benzyl-*N,N'*-diethylsulfamide (12).** According to the general procedure, 82 mg (1.10 mmol) of diethylamine was reacted with 1.00 mmol of **1** for 2 h to give 232 mg (96%) of **12**. Workup required EtOAc extraction (3 × 10 mL) of the product, the combined portions of which were washed with H_2O (6 × 10 mL), dried over $MgSO_4$, and concentrated. The crude product was purified by thick-layer chromatography on two 20 × 20 cm × 2 mm silica gel PF-254 (E. Merck) plates, eluting with $CHCl_3/CH_3OH$ (95:5), to give **12** as a colorless oil: TLC R_f 0.51; IR (film) 3.00 (N-H), 7.64 (S=O), 8.74 (S=O) μm; NMR ($CDCl_3$) δ 1.19 (t, 6 H, J = 7 Hz, CH_3), 3.26 (q, 4 H, J =7 Hz, $N(CH_2)_2$), 4.15 (d, 2 H, J = 6 Hz, $PhCH_2N$), 4.64 (br s, 1 H, NH), 7.34 (s, 5 H, Ph H). Anal. ($C_{11}H_{18}N_2O_2S$) C, H.

***N*-Benzyl-*N'*-phenylsulfamide (13).** According to the general procedure, 102 mg (1.10 mmol) of aniline was reacted with 1.00 mmol of **1**. After 44 h of reflux, considerable **1** was still present. Nevertheless, workup and recrystallization yielded 157 mg (60%) of **13** as colorless needles: mp 182–184 °C; IR (KBr) 3.05 (N-H), 7.70 (S=O), 7.80 (S=O) μm; NMR (acetone-d_6) δ 4.15 (d, 2 H, J = 6 Hz, $PhCH_2N$), 6.76–7.51 (m, 12 H, aromatic H, NH). Anal. ($C_{13}H_{14}N_2O_2S$) C, H.

Acknowledgment. We are grateful to Mr. G. McGarraugh for potentiometric studies.

Registry No. **1**, 74-282-81-8; **10**, 42731-71-5; **11**, 75420-75-6; **12**, 75420-76-7; **13**, 75420-77-8; benzylamine, 100-46-9; cyclohexylamine, 108-91-8; diethylamine, 109-89-7; aniline, 62-53-3.

(5) Burgess [Burgess, E. M.; Atkins, G. M., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 2502] has described a similar decomposition of $CH_3CH_2N{=}SO_2$ when generated at −78 °C and allowed to warm to ambient temperature.

Convenient Preparative Routes to 1,8-Bishomocubane, 1,8-Bishomocubanone, Snoutanone, and Homocubanone

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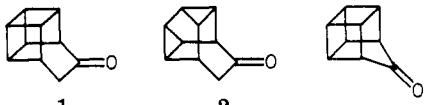
Among the various polycyclic molecules of current interest, the caged pentacyclic ketones, pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-9-one (1,8-bishomocubanone, **1**),[1] pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decan-9-one (snoutanone, **2**),[1] and pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one (homocubanone, **3**),[2] occupy positions of special vintage as they



1 **2** **3**

are interesting substrates for a variety of theoretical, mechanistic, and synthetic studies, and they also serve as ready precursors for several derivatives of these ring systems. We describe here new, short and preparatively useful routes to **1** and **2** and a modified economical preparation of **3**, all of which represent significant improvements over existing literature methods. A simple three-step preparation of parent 1,8-bishomocubane[3] (**4**) from cyclooctatetraene (COT) is also described.

The starting material for the preparation of **1** and **2** was the readily available[4] COT–acrylonitrile adduct **5**. Photolysis of **5** under our conditions (see the Experimental Section) proceeded smoothly to furnish intramolecular [$_\pi2_s + {}_\pi2_s$] addition product **6** in 70% yield.[5] The caged cyano compound **6** served as the common precursor for the preparation of **1**, **2**, and **4** (Scheme I). When **6** was subjected to oxidative decyanation according to the procedure of Watt,[6] 1,8-bishomocubanone (**1**) was obtained in nearly 50% yield. For the preparation of **2** it was essential to effect the transition metal catalyzed rearrangement[7] of **6**.

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(4) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **33**, 2211 (1968).
(5) Photolysis of **5** has been briefly reported by R. R. Sauers, A. D. Rousseau, and B. Byrne, *J. Am. Chem. Soc.*, **97**, 4947 (1975). However, they obtained only 36% yield after long (125 h) irradiation.
(6) S. J. Selikson and D. S. Watt, *J. Org. Chem.*, **40**, 267 (1975).
(7) For a detailed study of Ag(I)-catalyzed rearrangements of 1,8-bishomocubanes, see L. A. Paquette and R. S. Beckley, *J. Am. Chem. Soc.*, **97**, 1084 (1975).

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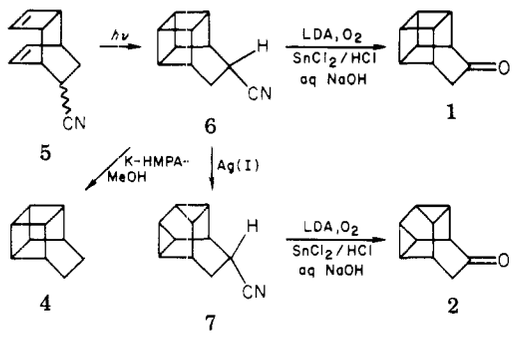
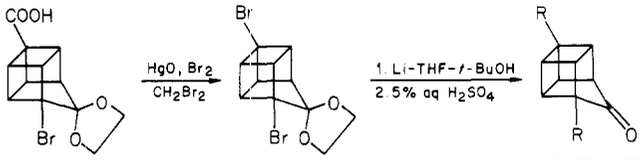
Scheme I



Passage of pentacyclic **6** through a silica gel column impregnated with $AgNO_3$ led to quantitative formation of **7**. Oxidative decyanation[6] furnished snoutanone (**2**) in over 50% yield. Finally, reductive decyanation[8] of **6** with potassium in HMPA–MeOH and direct sublimation of the product furnished 1,8-bishomocubane (**4**) in 65% yield in only three steps from COT.

Homocubanone **3** was prepared from the readily available[9] homocubane carboxylic acid derivative **8**. Halo-



8 **9** **3**, R = H; **10**, R = D

decarboxylation of **8** yielded the dibromo ketal **9** which was dehalogenated[10] with Li–THF–*t*-BuOH and hydrolyzed with acid to yield **3**.[11] All the steps from **8** to **3** proceeded in over 90% yield. The procedure for obtaining **3** from **8** is particularly efficacious for preparing labeled **3** required in mechanistic studies.[12] Thus, reaction of **9** with Li–THF–*t*-BuOD led to the formation of homocubanone-d_2 (**10**; d_2 = 49%, d_1 = 35%, d_0 = 16%) in high yield.

Structures of all new compounds obtained in this study were assigned on the basis of spectral data summarized in the experimental section. Identity of known compounds was established through comparison of spectral characteristics as reported in the literature. ^{13}C NMR data for compounds reported here are summarized in Table I.

Experimental Section

All melting points were recorded on a Buchi SMP-20 apparatus and are uncorrected. IR, ^1H NMR (100 MHz) and ^{13}C NMR (25 MHz) spectra were recorded on Perkin-Elmer-297 spectrophotometer, JEOL MH-100 spectrometer, and JEOL FX-100 spectrometer, respectively. The chemical shifts are reported on the δ scale relative to internal Me_4Si. GLC analyses were performed on a HP-5830A instrument on a Carbowax 20M column (6 ft × $^1/_8$ in.) at column temperatures of 130 and 200 °C and the samples for which data are reported had purity above 95%. Moisture-sensitive reactions were conducted by using standard syringe techniques under a dry nitrogen atmosphere. All solvent extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator.

Table I. ^{13}C NMR Chemical Shifts for Compounds 1–4, 6, 7, and 9

compd	chemical shift,[a] δ
1	211.4 (s), 47.8 (d), 44.5 (d), 43.1 (d), 41.7 (2 C, d), 39.0 (2 C, d), 36.8 (d), 36.3 (t)
2	214.4 (s), 48.2 (d), 38.1 (t), 35.1 (d), 31.6 (2 C, d), 31.4 (2 C, d), 30.4 (2 C, d)
3	45.7 (2 C), 44.1 (2 C), 39.2 (4 C), carbonyl carbon not seen
4	43.6 (2 C, d), 39.8 (4 C?, d), 32.6 (2 C, d), 16.8 (2 C, t)
6	123.1 (s), 43.7 (d), 43.2 (d), 38.9 (d), 38.4 (d), 38.3 (d), 36.8 (d), 33.3 (d), 30.5 (d), 22.0 (t), 19.3 (d)
7	124.2, 34.5, 29.9, 29.7, 29.3, 29.1, 27.0, 26.2, 25.9, 25.7, 22.6
9	124.5, 66.0 (2 C), 64.0, 56.9, 51.5 (3 C), 51.3, 48.5, 42.8

[a] All spectra were recorded in $CDCl_3$ and off-resonance multiplicities, when recorded, are given in parentheses.

9-Cyanopentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (6). A solution of 9-cyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene[4] (1.5 g, 9.56 mmol) in 850 mL of benzene which contained 17 mL of acetone was purged with a slow stream of nitrogen for 20 min. The solution was then irradiated with a 450-W Hanovia medium-pressure mercury-vapor lamp with a Vycor filter for 35 h. Removal of solvent and filtration through a silica gel (20 g) column, using 1:1 benzene–petroleum ether as eluant, yielded 1.1 g of oil, which on short path distillation yielded 1.05 g (70%), bp 120 °C (bath, 1.2 mm), of **6**: IR (neat) 2240 cm^{-1} (CN); ^1H NMR (CCl_4) δ 2.5–3.5 (m, 9 H), 1.8 (m, 2 H).

Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-9-one (1). To a solution of lithium diisopropylamide (6 mmol) in 10 mL of dry THF (made by adding 5 mL of 1.6 M *n*-butyllithium in hexane to a stirred solution of diisopropylamine (600 mg, 6 mmol) in 5 mL of dry THF at −78 °C) was added 9-cyanopentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (630 mg, 4 mmol) in 5 mL of dry THF at −78 °C. Dry oxygen gas was bubbled at a moderate rate into the lithionitrile solution for 40 min at −78 °C. The reaction was quenched with 20 mL of 1 M stannous chloride in 2 M HCl and allowed to stir for 2 h at ice temperature. The reaction mixture was diluted with water (50 mL) and extracted with ether (3 × 25 mL). Washing of the ether extract with 1 M NaOH and concentrating yielded an oily residue. Direct sublimation at 80 °C (5 mm) afforded 290 mg (50%) of **1**, leaving behind a small uncharacterized solid residue. Recrystallization of the sublimed solid from petroleum ether gave the crystalline compound: mp 82–83 °C (lit.[1] mp 85–87 °C); IR (CCl_4) 1710, 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.1–3.7 (m, 8 H), 2.13 (s, 2 H).

Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (4). To finely cut potassium (156 mg, 4 mmol) in dry ether was added successively 9-cyanopentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (314 mg, 2 mmol), dry methanol (70 mg, 2.2 mmol), and hexamethylphosphoramide (0.75 mL) at ice temperature with magnetic stirring. Stirring was continued and the reaction mixture was allowed to warm to room temperature over a period of 30 min. After being stirred for another 30 min, the reaction mixture was cooled in an ice bath and quenched with ice water (1 mL). Dilution with water, extraction with ether (2 × 25 mL), and direct sublimation [50 °C (20 mm)] yielded 170 mg (65%) of **4**. Recrystallization from methanol gave **4** as sugary crystals: mp 105 °C (lit.[3] mp 102.5–104.5 °C); ^1H NMR (CCl_4) δ 2.8–3.3 (m, 6 H), 2.6 (br s, 2 H), 1.35 (t, 4 H, J = 1.5 Hz).

9-Cyanopentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane (7). A solution of 9-cyanopentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (1.57 g, 10 mmol) in 5 mL of benzene was charged on a silver nitrate (15%) impregnated silica gel (25 g) column and left overnight. Elution with benzene and direct short-path distillation yielded 1.57 g (100%) of **7**: bp 110 °C (bath, 1.0 mm); IR (neat) 3040, 2240, 755, 795 cm^{-1}; ^1H NMR (CCl_4) δ 2.6 (m, 2 H), 2.03 (br s, 1 H), 1.1–2.2 (m, 8 H). Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.22; H, 7.10; N, 8.51.

Pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decan-9-one (2). To a solution of lithium diisopropylamide (3 mmol, prepared as described above) in 5 mL of dry THF was added 9-cyanopentacyclo-

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[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%).

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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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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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