Registry No.—1-Nitropropane, 10903-2; methylene chloride, 75-09-2; 1-nitrooctane, 629-37-8; nitroethane, 79-24-3.

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(3) A. L. Fridman, V. P. Ivshin, T. N. Ivshina, and S. S. Novikov, *Izv. Akad. Navk. SS SR, Ser. Khim.*, 2617 (1969).
(4) A mechanical stirrer is required.
(5) With the higher nitroparaffins it is advantageous to employ 25% methanol–75% water to achieve rapid solution.

Bicyclo[3.3.0]octane-2,6-dione and Bicyclo[3.3.0]octa-3,7-diene-2,6-dione

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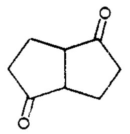
Several projects in this laboratory[1] have required substantial quantities of bicyclo[3.3.0]octane-2,6-dione (**1**) and the related dienedione **2**. Although these compounds have been known since 1934[2] and 1953,[3] respectively, the original



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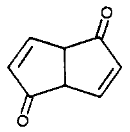

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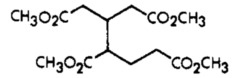
preparations, as well as some more recent procedures,[4] are unwieldy for large-scale operation. Therefore, we present here the details of our modified preparation of these versatile intermediates in molar quantities.

The synthetic sequence is outlined in Figure 1, and, as mentioned above, is based on the methods worked out by the Dauben group.[3,4] The free-radical induced coupling of dimethyl glutarate (**3**) to give tetraester **4** proceeds in only modest yield (ca. 50% based on recovered **3**), but is well suited for large (ca. 1 mol) runs. It is advisable to recrystallize the tetraester after distillation to remove some 15% of an impurity (presumably the isomeric ester **6**) which otherwise interferes in Dieckmann cyclization.



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The cyclization of **4** is best carried out with sodium methoxide in dimethyl sulfoxide (Me_2SO). Provided that all sources of hydroxide ion are excluded, this combination gives yields superior to those obtained previously with potassium *tert*-butoxide in *tert*-butyl alcohol.[4] Hydrolysis and decarboxylation of the resulting bisketo ester **5** are accomplished by heating with aqueous acid followed by extraction; because of an unfavorable partition coefficient, ether is a very poor solvent for this extraction, but the dione **1** is readily recovered using chloroform. If necessary, the dione may be purified by sublimation in vacuo; recrystallization is not recommended, as **1** tends to oil out, even when very pure.

The conversion of the saturated dione **1** into dienedione **2** was originally[3] carried out by chlorination, ketalization with ethylene glycol, double dehydrochlorination, and deketalization. The last procedure of the Dauben group[4b] paralleled this, employing the bromoketal. We experienced considerable difficulty with this route, finding bromination of the bisenol acetate capricious, and the ketalization and elimination steps very slow. We have employed instead the sequence used by Eaton in some related systems,[5] and found it very satisfactory.

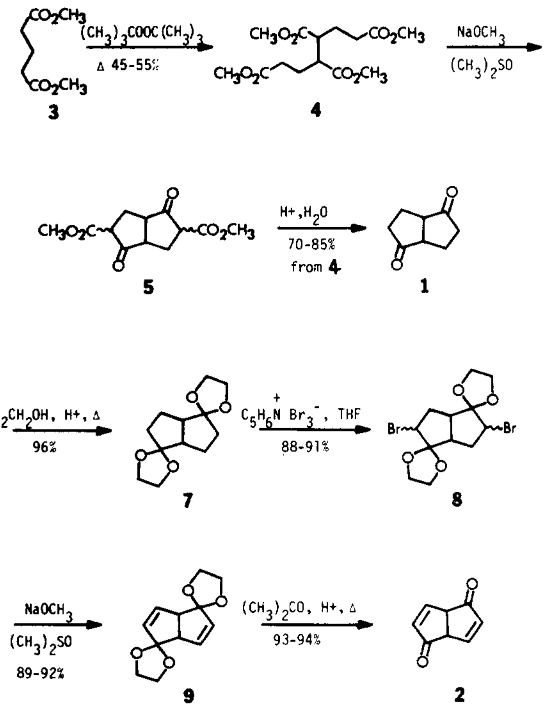

Figure 1. Improved synthesis of bicyclo[3.3.0]octa-3,7-diene-2,6-dione (**2**).

Ketalization of dione **1** with ethylene glycol proceeds smoothly and in nearly quantitative yield. The oily diketal is then brominated with pyridinium tribromide in tetrahydrofuran at low temperature (if the reaction is carried out at or near room temperature considerable polymer is formed, and the product can be purified only with difficulty). The dibromo diketal **8** may also be obtained directly by brominating **1** in ethylene glycol,[6] but this method is suitable for small-scale runs only. Although double dehydrobromination of **8** with ethanolic potassium hydroxide[4] requires refluxing for several days for complete reaction, the elimination may be effected in several hours with sodium methoxide in Me_2SO. Finally, ketal exchange with acetone afforded dienedione **2**.

By means of these procedures we have obtained quantities of both diketones sufficient to permit their use as starting materials for other syntheses. The preparations are reasonably rapid and efficient and, provided the usual precautions are taken, free from hazard. There is no reason to suppose that they could not be scaled up several fold over the amounts specified in the Experimental Section, provided suitably sized equipment is at hand.

Experimental Section

General. All melting points were measured in open capillaries with a Thomas-Hoover apparatus and are uncorrected; boiling points are also uncorrected. Combustion analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Unless noted otherwise, reagents and solvents were reagent-grade materials used as received.

Proton nuclear magnetic resonance (NMR) spectra were run on Varian A-60, A-56/60, and T-60 instruments (60 MHz). Chemical shifts are reported in parts per million downfield of internal tetramethylsilane (δ 0.0). Infrared spectra were measured on a Perkin-Elmer Model 137 spectrophotometer. Liquid samples were examined as neat films, and solids as Nujol mulls. All gas chromatographic separations were achieved using an F and M Model 700 chromatograph equipped with a thermal conductivity detector. Helium was used as the carrier gas at flow rates of 70–80 mL/min; an injector temperature of 240 °C and a detector temperature of 270 °C were used

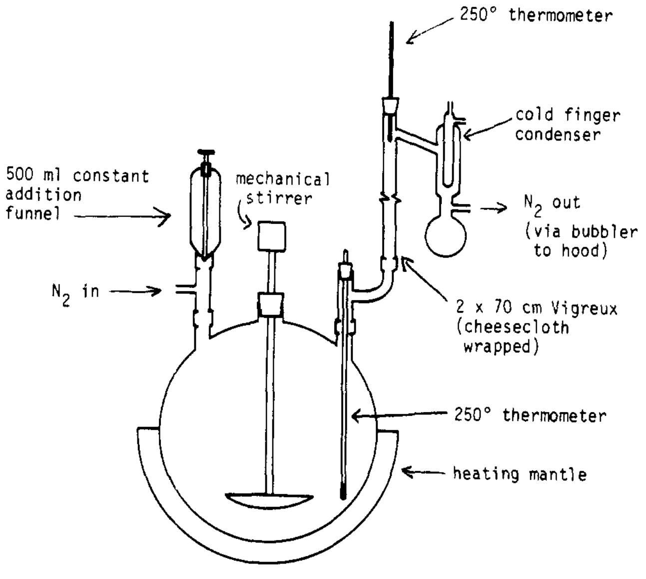

Figure 2. Apparatus for preparation of tetraester 4.

in all cases. The compositions reported were calculated from the peak areas (determined by triangulation) without corrections for differing detector responses. The columns employed were 6 ft × $^1/_4$ in. aluminum columns packed with the following materials: column A, 4% QF on 60–80 mesh Chromosorb G, acid and base washed and silanized; column B, 5% Carbowax 20M on 60–80 mesh Chromosorb G, acid and base washed and silanized; column C, 4% OV-17 on 60–80 mesh Chromosorb G, acid and base washed and silanized; column D, 1% SE-30 on 60–80 mesh Chromosorb G (untreated).

Dimethyl Glutarate (3). A mixture of glutaric anhydride (Aldrich, technical grade, 70% stated purity, 2.5 kg), methanol (2 L), and *p*-toluenesulfonic acid (1–2 g) was refluxed for 20–30 h. The reaction mixture was cooled, diluted with 1 L of water, made slightly basic by the addition of 10% sodium hydroxide solution, and extracted with ether (4 × 1 L). The combined ether layers were washed with water and saturated aqueous sodium chloride solution, dried over Drierite, and freed from solvent on the rotary evaporator. Distillation of the residue afforded impure dimethyl glutarate, bp 90–110 °C (17 mm). This material was redistilled through a 1-m Vigreux column, and the fraction boiling at 99–101 °C (17 mm) was collected. This product, a water-white oily liquid, was ca. 99.5% pure by GC (column A, 150 °C); yields were in the range 45–55%.

The aqueous solution from the above extraction was acidified with hydrochloric acid. Extraction of this mixture with ether afforded, after removal of the solvent, very crude momomethyl glutarate, which was combined with the glutaric anhydride for reuse.

Tetramethyl Hexane-1,3,4,6-tetracarboxylate (4). Free Radical Induced Coupling of Dimethyl Glutarate. This procedure is a slight modification of those of Osborne[4a] and Simpson.[4b] The reaction vessel was a 5-L three-necked flask equipped as shown in Figure 2. The flask was charged with 2500 mL of dimethyl glutarate (DMG), which was heated to boiling, with stirring, while nitrogen was passed through the apparatus. After 15 min of boiling, the DMG was cooled to 175 °C, and the nitrogen flow was adjusted to 45–50 mL/min. A mixture of di-*tert*-butyl peroxide (Columbia, 400 mL, ca. 2.17 mol) and DMG (160 mL) was then added to the vigorously stirred DMG, maintaining the liquid temperature at 170–175 °C; the addition rate was 1 mL/min. After addition was completed, heating was continued until gas evolution ceased (this was determined by temporarily stopping the nitrogen flow and inspecting the gas bubbler at the outlet of the system); this typically required an additional hour. When no more gas was evolved, the contents of the flask were rapidly heated to vigorous boiling until DMG (bp 214 °C) began to distill over.

The flask and contents were allowed to cool overnight, and the reaction mixture was transferred to a 5-L round-bottom flask. Unreacted DMG was then removed by vacuum distillation through a 50-cm Vigreux column; everything boiling up to 140 °C (17 mm) was collected in one fraction. The volume of recovered DMG was 2180 mL, so 480 mL (ca. 520 g, 3.23 mol) of DMG had been consumed.

The residue in the pot was cooled to around 80 °C, and transferred while hot to a 1-L round-bottom flask. Distillation was then continued through the 50-cm Vigreux; three fractions were collected: fraction 1, 20 g, bp 80–135 °C (0.02 mm); fraction 2, 290 g, bp 135 (0.02 mm)–155 °C (0.03 mm) [most of this material boiled at 140–143 °C (0.02 mm)], and fraction 3, 20 g, bp 155–180 °C (0.03 mm). The dark pot residue was discarded.

All of these fractions eventually solidified to give mushy white crystals. Fraction 2 contained about 85% of the desired product and about 15% of an additional compound (two barely separated peaks by GC on column A, 210 °C). Solution of fraction 2 in an equal volume of warm methanol and cooling to 10 °C afforded 165 g of white crystals (a mixture of needles and tablets). Two more crops, 54 and 6.5 g, were obtained by cooling the mother liquor to −10 °C and then to −60 °C. Fractions 1 and 3 were combined and crystallized in the same manner to give 11 g more (two crops, 10 and −60 °C). Thus, the total recrystallized product came to 236.5 g (0.745 mol). This corresponds to a yield of ca. 46% based on the DMG consumed, or 34% based on the di-*tert*-butyl peroxide.

Subsequent runs were made in the same manner, using the recovered DMG; after four or five batches, the DMG was refractionated, as described previously, to remove the impurities which had accumulated. The apparatus and still were not cleaned between runs, so as to minimize losses due to holdup. A number of preparations afforded recrystallized 4 in yields of 42–55% based on reacted DMG.

The mother liquors from the recrystallization of several preparations could be combined and processed as above to obtain an additional amount of pure tetraester 4. The broad melting range of the recrystallized tetraester (48–59 °C) is undoubtedly due to the presence of a mixture of the meso and *dl* diastereomers. The other data on this mixture are in complete agreement with structure 4: IR (neat melted) 5.75 μm; NMR (δ, CCl_4) 3.70 (6 H, s), 3.65 (6, H, s), 2.68 (2 H, br t, J = 4 Hz), 2.50–2.06 (4 H, m), 1.84 (4 H, br m).

Bicyclo[3.3.0]octane-2,6-dione (1). Dieckmann Cyclization of Tetraester 4, and Hydrolysis-Decarboxylation of the Product, Keto Ester 5. NB. The success of this procedure depends crucially upon the strict exclusion of water and other sources of hydroxide ion. The use of dry glassware, dry dimethyl sulfoxide (Me_2SO), and fresh sodium methoxide is essential; if these precautions are not taken, the yield drops substantially, even to the point of no product being formed. It should be noted that even freshly opened bottles of commercial reagent grade Me_2SO usually gave unsatisfactory results. Me_2SO was purified by stirring with calcium hydride for several days, then vacuum distillation from the same drying agent: bp 77–78 °C (15 mm).

A 1-L three-necked flask was fitted with a mechanical stirrer, addition funnel, thermometer, and provision for an inert atmosphere. The apparatus was then flame dried while it was evacuated. Sodium methoxide, *freshly opened* (60 g, 1.1 mol), and dry Me_2SO (ca. 300 mL) were then added, and a nitrogen atmosphere was established by repeated cycles of evacuation and bleeding in nitrogen. Tetraester 4 (159 g, 0.50 mol), dissolved in ca. 150 mL of warm Me_2SO, was then added to the stirred slurry of sodium methoxide. Addition took 15 min, during which the internal temperature rose to 50–60 °C. An additional portion of sodium methoxide (40 g, 0.74 mol) was then added. The reaction mixture, which had become deep orange during the ester addition, was then heated at 70–80 °C for 1.5 h. The nearly black mixture was then cooled to 20–25 °C with an ice bath, and *ice-cold* 6 M hydrochloric acid (320 mL) was added slowly, with continued stirring. Ice bath cooling was used to keep the temperature below 30 °C. As the acid was added, the mixture lightened in color, becoming yellow-brown and finally pink with a finely divided solid precipitate. The final slurry was poured into 2.5 L of ice water, and the pH was checked to make certain it was acidic. When the temperature of this mixture reached 10 °C the solid was collected by filtration through a *large* Buchner funnel, washed several times with cold water, washed once with cold methanol–water (1:1), and sucked as dry as possible. The crude bisketo ester was then dried, first at room temperature and finally in an oven at 85–90 °C. The oven drying led to considerable sintering and some darkening of the initially yellow or pink, powdery product, but did no harm; the sintering was in fact beneficial in the next step. The crude keto ester 5 weighed 109.5 g (86.3% crude) and showed mp 91–98 °C dec. Further purification was not necessary, but could be achieved by crystallization from methanol (5 mL/g) in 80% recovery. The recrystallized product melted at 93–96 °C; a second recrystallization, this time from acetone–hexane, gave colorless prisms, mp 92–93 °C (lit.[4a] 90.4–92.4 °C).

The entire crude product from the above Dieckmann cyclization was added to 300–400 mL of 6 M hydrochloric acid, containing one small drop of Dow-Corning "Antifoam C" defoamer, in a 2-L Erlenmeyer flask. Several Carborundum boiling stones were added, and the mixture was heated on the steam bath with frequent swirling (gas evolution and foaming!); the temperature was kept below 70 °C, as considerable darkening occurred at higher temperatures, and the foaming became inconveniently vigorous. When gas evolution had ceased (typically, after about 1 h of heating), the solution was cooled and filtered with suction through two thicknesses of filter paper. The filtrate was then extracted six times with 200-mL portions of chloroform. The chloroform layers were combined and washed with 5 M aqueous sodium hydroxide solution (2 × 25 mL), and concentrated to ca. 500 mL by distillation; this also effected azeotropic drying of the solution. The chloroform solution was filtered through a Dierite cone (to catch the fine particles). Removal of the solvent on the rotary evaporator gave a golden yellow oil, which slowly solidified to a pale yellow mass. The yield of crude dione 1 was 56.1 g (96.1% based on the crude keto ester; 82.9% from tetraester 4), yellowish granules, mp 43–46 °C. Again, further purification was not necessary. If desired, purer material could be obtained by sublimation [35–40 °C (0.01 mm)] onto a cold finger kept at 0 °C. Recovery was about 97%. The sublimed product was in the form of blocky crystals, mp 45.1–46.3 ° (lit.[4b] 46–46.5 °C) with the expected spectral properties: IR (Nujol) 5.73 μm; NMR (δ, CCl_4) 2.90 (2 H, br s), 2.20 (8 H, br s).

2,2,6,6-Bis(ethylenedioxy)bicyclo[3.3.0]octane (7). Ketalization of Bicyclooctanedione 1. The crude dione (209 g, 1.5 mol) was added to a mixture of ethylene glycol (200 mL, ca. 3.95 mol, 32% excess), *p*-toluenesulfonic acid hydrate (3.8 g, 0.02 mol), and benzene (1.5 L). This mixture was refluxed with separation of water (Dean–Stark trap, 64 mL, 118%) and magnetic stirring for 44 h. Nearly all of the water distilled over during the first 12 h. The brownish solution was cooled and washed as follows: 1 × 100 × 200 mL of saturated aqueous sodium bicarbonate, 2 × 200 mL of water, and 2 × 100 mL of saturated aqueous sodium chloride solution. The combined aqueous washings were extracted four times with 200-mL portions of ether, which were combined and washed once with saturated sodium chloride solution. This ether extract, combined with the original benzene layer, was filtered through a Drierite cone. Removal of the solvent on the rotary evaporator gave a brownish, oily liquid, which was distilled in vacuum. The fraction, bp 93–95 °C (0.15 mm), homogeneous by GC (column A, 170 °C; column B, 190 °C), was collected to give 327 g (96.5%) of a colorless, oily liquid. Repeated fractional freezing of this liquid in an ice–acetone bath gave an analytical sample. The spectra of this purified material, which were superimposable on those obtained from the distillate, were as follows: IR (neat) 3.41, 3.49, 6.82, 7.47, 8.24, 8.6–9.15, 9.64, 10.53 μm; NMR (δ, CCl_4) 3.87 (8 H, s), 2.37 (2 H, br m), 1.62 (8 H, br m).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.67; H, 8.02.

Other preparations, on 0.2–0.6-mol scales, gave yields of 96.1–96.4%. In view of the ca. 97% purity of the crude dione 1, the yield must be close to quantitative. Other boiling points observed were 100 °C (0.2 mm), 88 °C (0.05 mm), and 84 °C (0.015 mm).

2,2,6,6-Bis(ethylenedioxy)-3,7-dibromobicyclo[3.3.0]octane (8). Bromination of Ketal 7. Pyridinium tribromide was prepared according to Fieser and Fieser,[7] starting with approximately 1 lb of bromine and scaling the other reactants accordingly. During the recrystallization of the product from acetic acid, the mixture was stirred frequently to keep the crystals small. We and others[8] have found that finely divided tribromide gives better results than coarse material. Yields of the purified tribromide were in the range 72–78%.

The diketal 7 (45.2 g, 0.2 mol) was dissolved in dry tetrahydrofuran (400 mL, distilled from CaH_2) in a 1-L three-necked flask equipped with a mechanical stirrer, a drying tube, and a stopper. This solution was cooled, with stirring, to ca. −70 °C in a dry ice–acetone bath, and pyridinium tribromide (140 g, 0.438 mol) was added in one portion. The mixture, which rapidly decolorized, was stirred at ca. −70 °C for 1 h, then allowed to warm to room temperature. The pale yellow suspension was then poured slowly into 2.5–3 L of vigorously stirred cold water, whereupon the product precipitated. After 5 min more stirring, the solid was collected by filtration, washed repeatedly with water, and sucked fairly dry. This yellowish product was then covered with methanol (ca. 200 mL), the lumps were broken up, and the stirred mixture was gently boiled for a few minutes. It was then cooled to −10 °C for several hours, and the white product was collected, washed once with cold methanol, and air dried to give 69 g (90%) of white crystals (needles and granules), mp 152–156 °C (sinters 128 °C, further softens 142–145 °C, with gradual darkening from 128 °C on). Other runs on a similar scale (0.2–0.25 mol) gave yields in the range 88–91%.

2,2,6,6-Bis(ethylenedioxy)bicyclo[3.3.0]octa-3,7-diene (9). Dehydrobromination of Bromoketal 8. The methanol-washed mixture of isomeric bromo ketals (87 g, 0.227 mol) prepared from 7 was added in one portion to a stirred slurry of sodium methoxide (73.5 g, 200% excess) in dimethyl sulfoxide (400 mL) in a 1 L, three-necked flask equipped with a mechanical stirrer, a thermometer, and a gas bubbler. Occasional cooling (ice bath) was used to keep the reaction temperature below 60 °C. After the exothermic reaction had ceased (ca. 30 min) the mixture was heated to 70 °C for 2 h. It was then cooled to room temperature and poured into 2.5 L of stirred water and ice and the flask was rinsed with an additional 100 mL of water. Solid sodium chloride was added to nearly saturate the solution, and the crude solid product was collected by filtration. The filtrate was then extracted eight times with 500-mL portions of ether, each of which was roughly dried by washing with 50 mL of saturated sodium chloride, and evaporated as it was obtained. The residue from these extracts was combined with the original solid product, dissolved in cyclohexane (ca. 1200 mL), and refluxed with water separation (Dean–Stark trap). When water ceased to distill over, the hot cyclohexane solution was filtered, concentrated by distillation to a volume of about 500 mL, and allowed to cool. The product, 44.8 g (89%) of fine colorless needles, mp 101–102 °C, was then collected. Concentration of the mother liquor afforded an additional crop (1.5 g, 3%) of slightly yellowish needles, mp 97–100 °C. Other runs on the same scale gave total yields of 89–93%.

Bicyclo[3.3.0]octa-3,7-diene-2,6-dione (2). Deketalization of Ketal 9. The diene diketal 9 (44.5 g, 0.2 mol) and sulfosalicylic acid (0.3 g) were dissolved in acetone (500 mL) with gentle warming, and the solution was allowed to stand at room temperature for several hours. The acetone and its ethylene ketal were removed on the rotary evaporator. The residue was taken up in acetone, allowed to stand for 30 min, and the volatile material again removed. After a third acetone treatment, the solid residue was sublimed at 70 °C (0.01 mm) onto a carbon tetrachloride–slush cooled condenser, yielding 25.2 g (94%) of white, blocky crystals, mp 76.5–78.5 °C. Recrystallization of this material, although not necessary, could be achieved using cyclohexane as solvent. This gave colorless or white needles, mp 78–79 °C (lit.[3] 78–79.5 °C), in nearly quantitative recovery (three crops): IR (Nujol) 5.88 (strong and broad), 6.35 μm; NMR (δ, CCl_4) 7.66 (2 H, d of m, J = 5.6 Hz), 6.08 (2 H, d of d with additional fine structure, J = 5.6 Hz, J' = 1.4 Hz), 3.67 (2 H, m).

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Registry No.—**1,** 17572-87-1; **2,** 4945-71-5; **3,** 1119-40-0; *meso*-**4,** 63569-68-6; *dl*-**4,** 63569-69-7; **5,** 63569-70-0; **7,** 63569-71-1; **8,** 63569-72-2; **9,** 63569-73-3; glutaric anhydride, 108-55-4.

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Persistent Free Radicals from the Reaction of Sulfenamides with Tetracyanoethylene

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It was reported earlier that tetracyanoethylene reacts with sulfenamides but no identification of the products of the reaction was given.[1] This note reports the observation of persistent radicals in these reaction mixtures. The radicals were observed when degassed benzene, dichloromethane, or tetrahydrofuran solutions of the sulfenamides[2] were mixed with