Ethyl 6-Hexyl-2,4-dihydroxybenzoate.—Repeated extraction of the residue (R = *n*-hexyl) described in the above 5-alkylresorcinol preparation, with boiling hexane followed by refrigeration, left behind an insoluble black oil. The combined hexane solutions while still warm were extracted with water, dried with magnesium sulfate, filtered, and chilled slowly in a Dry Ice bath with occasional scratching. Crystals finally separated. Three recrystallizations from hexane gave a small amount of the ester, mp 74–75°.

Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.33; H, 8.28.

Ethyl 6-Undecyl-2,4-dihydroxybenzoate.—This residue (R = *n*-undecyl) described in the above 5-alkylresorcinol preparation was dissolved in 250 ml of hot hexane. On refrigeration, 10.15 g of crystalline product separated. The mother liquor gave an additional 4.40 g of crystals on concentration, thus giving a yield of 14.55 g (41%). Two recrystallizations from hexane gave an analytical sample, mp 67.5–68.5°.

Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.39; H, 9.59. Found: C, 71.13; H, 9.67.

Ethyl 2-Carbethoxy-3,5-dihydroxyphenylbenzoate.—The residue (R = carbethoxymethyl) as described in the above 5-alkylresorcinol preparation had solidified. It was recrystallized from 175 ml of hot 70:30 hexane–dichloromethane, giving 11.5 g (43%) of tan needles of product. Recrystallization (same solvent system, activated charcoal used) gave 9.5 g of white needles, mp 107.0–107.5°. Another recrystallization gave an analytical sample, mp 107.5–108.0° with prior softening (lit.[7] mp 108°).

Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.06; H, 5.98.

Registry No.—Triethyl phosphonoacetate, 867-13-0; ethyl 6-hexyl-2,4-dihydroxybenzoate, 34993-70-9; ethyl 6-undecyl-2,4-dihydroxybenzoate, 34991-68-9.

Acknowledgment.—The author is indebted to Professor Dietmar Seyferth for providing financial support (National Science Foundation Grant 6466X) and laboratory facilities.

[7] A. Kamal, A. Robertson, and E. Tittensor, *J. Chem. Soc.*, 3379 (1950).

A Convenient Synthesis of Barrelene

Gary N. Taylor

Bell Laboratories, Murray Hill, New Jersey 07974

Received March 8, 1972

Since its initial synthesis in 1960,[1] numerous papers have appeared concerning the spectra, reactivity, and properties of the homoconjugated triene barrelene (**1**). Recent work in this laboratory necessitated the preparation of some of this compound and bicyclo[2.2.2]octa-2,5-diene (**2**). The somewhat tedious synthetic routes to these materials[1–3] prompted a search for a more facile preparative route. The results of Hine and coworkers[4] suggested the opportunity for a three-step synthesis of both **1** and **2** if suitable alterations were made in the free-radical chlorination and dehydrohalogenation steps utilized in their procedure. In this fashion it has been possible to effect such a synthesis.

The first step is the ionic addition of hydrogen bromide to bicyclo[2.2.2]oct-2-ene, which affords 1-bromobicyclo[2.2.2]octane in yields exceeding 94%. Free-radical chlorination of the bromide using controlled excesses of sulfuryl chloride affords mixtures of polychlorobromobicyclo[2.2.2]octanes which may be biased in favor of the monochloro or polychloro derivatives depending on the amount of sulfuryl chloride employed. The final step is the low-temperature dehydrohalogenation of the polyhalobicyclo[2.2.2]octane mixture using potassium *tert*-butoxide in DMSO. Use of this reagent allows the multiple elimination reaction to be conducted at temperatures below the decomposition point of barrelene but still in reasonable yields. Separation and collection of the products by glpc using a temperature-programmed 10 ft × 0.375 in. Carbowax 20M column afforded pure samples of bicyclo[2.2.2]-octa-2,5-diene and barrelene. The yield of barrelene from bicyclo[2.2.2]oct-2-ene was approximately 2%. No attempts to maximize this yield were made, thereby indicating that overall yields in excess of those observed may be realized.

Experimental Section

1-Bromobicyclo[2.2.2]octane.—The procedure of Doering and Farber[5] was used. In a 1-l. three-necked flask was placed a solution of 75 g (0.70 mol) of bicyclo[2.2.2]oct-2-ene in 400 ml of ether. The stirred mixture was cooled to 10° and 65 g (0.80 mol) of hydrogen bromide was bubbled in at a rate such that a temperature of 15° was always maintained. After the addition was complete the stirred mixture was kept at room temperature for 1 day. Then it was poured into 1 l. of ice water. The layers were separated and the aqueous portion was extracted three more times with 100 ml of ether. The combined ether extracts were washed with saturated sodium bicarbonate solution until the washings were basic and then with 200 ml of saturated sodium chloride solution. After drying ($MgSO_4$), evaporation of the solvent afforded 124 g (94%) of white, crystalline 1-bromobicyclo[2.2.2]octane, nmr (CCl_4) τ 5.76 (m, 1 H, HCBr) and 7.3–8.9 (m, 12 H).

Chlorination of 1-Bromobicyclo[2.2.2]octane.—A modified method of Hine and coworkers[4] was used. In a 500-ml one-necked flask was placed 124 g (0.66 mol) of bicyclooctyl bromide, 135 g (1.00 mol) of sulfuryl chloride, and 0.24 g of benzoyl peroxide. The reaction vessel was purged with nitrogen and the mixture was heated at reflux until the temperature of the mixture reached 190°. After cooling, the black residue was dissolved in 600 ml of ether. The resulting solution was washed twice with 50 ml of saturated sodium bicarbonate solution and twice with 100 ml of saturated sodium chloride solution. Drying ($MgSO_4$) and solvent removal afforded a residue which upon distillation gave two major fractions: (a) bp <130° (19 mm), 49 g (40%), judged from nmr to be mostly unreacted starting material; (b) bp 130–165°, 60 g, a mixture of polychlorobromobicyclo[2.2.2]octanes. Fraction b was used without further purification in the dehydrohalogenation step.

Bicyclo[2.2.2]octa-2,5-diene and Bicyclo[2.2.2]octa-2,5,7-triene.—In a dry nitrogen-flushed 500 ml three-necked flask were placed 56 g (0.50 mol) of potassium *tert*-butoxide and 150 ml of dry dimethyl sulfoxide. Then 25 g of the polychlorobromobicyclo[2.2.2]octane fraction (b) in 50 ml of dimethyl sulfoxide was added dropwise over a 10-hr period while the temperature was maintained at 40°. Upon completion of the addition the mixture was heated at 40° for an additional 1 hr, cooled, and poured into 1 l. of ice water. The aqueous solution was extracted with three 100-ml pentane portions and the combined extracts were washed twice with 50 ml of saturated sodium chloride solution. Drying ($MgSO_4$) and removal of the pentane by distillation through a 30-cm column packed with glass helices gave a 15-g residue which upon distillation afforded 5.0 g of a colorless liquid, bp 90–120°

---

[1] H. E. Zimmerman and R. M. Paufler, *J. Amer. Chem. Soc.*, **82**, 1514 (1960).

[2] H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969).

[3] C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

[4] J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *J. Amer. Chem. Soc.*, **77**, 594 (1955).

[5] W. v. E. Doering and M. Farber, *ibid.* **71**, 1514 (1949).

(155 mm). Glpc analysis using a 10 ft × 0.375 in. Carbowax 20M column programmed at 1°/min from 80 to 105° after a post injection delay of 20 min and at 10°/min from 105 to 160° with an upper limit delay of 20 min revealed 4 major and 12 minor components using a helium flow of 56 ml/min. Nmr spectra of the major components eluting at 27.5 and 42 min showed them to be bicyclo[2.2.2]octa-2,5-diene [nmr (CCl_4) τ 3.90 (p, 4 H, CH=), 6.50 (m, 2 H, bridgehead), and 8.78 (m, 4 H, bridge)][6] and bicyclo[2.2.2]octa-2,5,7-triene [nmr (CCl_4) τ 3.50 (structured pentet, 6 H, CH=) and 5.40 (m, 2 H, bridgehead)],[2] respectively. The two other major eluents had retention times of 54.5 and 60.5 min and were not further characterized. Two of the minor components eluting at 13 and 20 min were identified as benzene and bicyclo[2.2.2]oct-2-ene, respectively. The percentages of 1 and 2 estimated on the basis of total eluted materials were approximately 17 and 32%. Preparative glpc separation of 2.0 g of distillate afforded 0.24 g of barrelene for a yield of 2% based on bicyclo[2.2.2]octene.

Equipment.—Nmr spectra were taken using a Jeol C-60HL spectrometer. Analytical and preparative glpc were conducted using a Hewlett-Packard Model 5750 vapor phase chromatograph equipped with a Model 5797 A collection unit.

Registry No.—Barrelene, 500-24-3; 1-bromobicyclo-[2.2.2]octane, 7697-09-8.

---

[6] K. Lori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida *Can. J. Chem.*, **42**, 926 (1964).

An Improved Preparation of 1,3-Cyclopentanedione

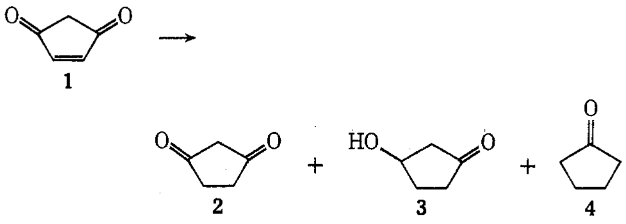
John M. McIntosh* and Pierre Beaumier

Department of Chemistry, University of Windsor, Windsor, Ontario, Canada

Received April 6, 1972

During the course of other investigations, we required a source of relatively large amounts of 1,3-cyclopentanedione (2). Although this compound and its alkylated derivatives have been used in the synthesis of many materials of varying degrees of complexity,[1] methods for its preparation, particularly on a large scale, are limited. The most widely quoted method[2] suffers from large solvent volumes, difficult isolation, and erratic yields. Other methods give unacceptably low yields.[3] Catalytic hydrogenation and zinc–acetic acid reduction of 4-cyclopentene-1,3-dione (1) have been reported.[4] Low yields of 2 were obtained, but the choice of catalyst and reaction conditions for these reactions did not appear to be optimal. Therefore we decided to reinvestigate the reduction of 1 as an attractive route to 2.

It is well established that the selective hydrogenation of olefins in the presence of carbonyl functions occurs best when palladium rather than platinum catalysts are employed.[5] Whereas the use of Adams' catalyst in the hydrogenation of 1 afforded only 2% of 2 in addition to large amounts of 3 and 4,[4] employing a palladium catalyst resulted in the continuous absorption of in excess of 1 equiv of hydrogen and the formation of a 3:2 mixture of 2 and 3, which could be separated by distillation. No cyclopentanone was formed. Variation of the solvent from 95 to 75% ethanol drastically reduced the rate of reduction, but did not change the product distribution substantially.



The reduction of conjugated diketones with zinc in acetic acid is a well-documented process,[6] but the reported yield[4,7] of 2 from the reduction of 1 was low. We verified these results, but found that *the use of activated zinc*[8] afforded 2 *in 75–77% yield* after recrystallization. Purification by sublimation at pressures greater than 0.02 mm reduced the yield to less than 60%. The ready availability of 4-cyclopentene-1,3-dione[9] coupled with the simplicity and high yield of this reduction clearly make this route the method of choice for the preparation of 2. Whether the use of activated zinc in other reductions of this type will result in a similar improvement in yield remains to be investigated.

Experimental Section

Infrared spectra were taken on a Beckmann IR 12 spectrometer in chloroform solution; nmr spectra were recorded on a JEOLCO C60HL spectrometer in deuteriochloroform and are reported in parts per million from an internal standard (TMS = 0). Melting points are uncorrected. Microanalyses were performed by A. B. Gygli, Toronto, Ontario.

Catalytic Hydrogenation of 1.—To a solution of 1 g (0.01 mol) of 4-cyclopentene-1,3-dione[9] (1) in 25 ml of 95% ethanol was added a catalytic amount of 5% palladium on charcoal, and the mixture was hydrogenated at room temperature and pressure. Continuous absorption of hydrogen occurred until 1.6 molar equiv had reacted, at which point the reaction stopped. The solution was filtered free of catalyst, the solvent was evaporated, and the residue was distilled (90° bath temperature, 0.5 mm). Analysis of the distillate (0.37 g) by glc (8 ft × 0.25 in. 20% SE-30, 125°) showed the presence of two compounds, one of which had the same retention time as 2-cyclopentenone. No cyclopentanone was present. The spectra of the distillate identified the material as 3-hydroxycyclopentanone (3) from which the 2-cyclopentenone was formed by dehydration during glc analysis: ir 3610, 3450, 1737 cm^{-1}; nmr δ 4.6 (m, 1, CHOH), 3.58 (s, 1, -OH), 2.5–2.0 (m, 6). The residue from the distillation (0.6 g, 60%) was 1,3-cyclopentanedione (2), mp 151–152° (sublimed sample) (lit.[4] mp 149–150°).

Zinc Reduction of 1.—To a mixture of 500 ml of glacial acetic acid and 100 g (1.54 mol) of activated zinc[8] in a 2-l. flask equipped with a mechanical stirrer and maintained at 95° with an oil bath was added a solution of 20 g (0.21 mol) of 1 in 300 ml of glacial acetic acid over a period of 2 hr. The mixture was stirred at 95° for 1 hr, filtered, cooled to room temperature, and filtered again. Evaporation of the solvent at reduced pressure afforded a light yellow residue which gave 2 (15.5 g, 76%) on recrystallization from methanol–ethyl acetate (1:3) at −78°, mp 148–149°.

---

[1] (a) R. Zurfluh, E. N. Wall, J. B. Siddall, and J. A. Edwards, *J. Amer. Chem. Soc.*, **90**, 6224 (1968); (b) L. Velluz, J. Vallas, and G. Nomine, *Angew. Chem., Int. Ed. Engl.*, **4**, 181 (1965); (c) T. B. Windholz and M. Windholz, *ibid.*, **3**, 353 (1964).

[2] F. Merenyi and M. Nilsson, *Acta, Chem. Scand.*, **17**, 1801 (1963).

[3] J. H. Boothe, R. G. Williams, S. Kushner, and J. H. Williams, *J. Amer. Chem. Soc.*, **75**, 1732 (1953).

[4] C. H. DePuy and E. F. Zaweski, *ibid.*, **81**, 4920 (1959).

[5] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 10.

[6] See, for example, J. Elks, R. M. Evans, A. G. Long, and G. H. Thomas, *J. Chem. Soc.*, 451 (1954).

[7] H. O. House and G. Rasmusson, *J. Org. Chem.*, **28**, 27 (1963).

[8] J. W. Cornforth, R. H. Cornforth, G. Popjak, and I. Y. Gore, *Biochem. J.*, **69**, 146 (1958).

[9] G. H. Rasmusson, H. O. House, E. F. Zaweski, and C. H. DePuy, *Org. Syn.*, **42**, 36 (1962).