a small part of the several factors which control product formation.

It is evident from the results in Table I that the migratory aptitude of the angular alkyl group plays a dominant role. There still remain to be unravelled, however, those factors which control rearrangement of the angular methyl compound, **4a**.

The data in Table I were obtained from rearrangements at room temperature in acetic anhydride–sulfuric acid and at 51.5° in 20.6 *N* sulfuric acid. The effect of temperature on rearrangement of **4a** was measured. The ratio **7a**:**8a** was 85:15 at 100°. Rearrangement of **4a** in concentrated hydrochloric acid at 100° gave **5a** and **6a** in the ratio 15:85. These data show that temperature does not affect the trend in product formation. We assume that this will apply to rearrangements of **4b–d**, too.

### Experimental Section

**Materials.**—Commercially available 2-methylcyclohexanone (Aldrich Chemical Co.) and 2-propylcyclohexanone (K and K Laboratories) were used. 2-Ethyl- and 2-butylcyclohexanone were prepared by oxidation[13] of the corresponding cyclohexanol (K and K Laboratories). The four cyclohexanones were fractionally distilled before use in the annelation with 2-butyn-3-one (Farchan Research Laboratories). Annelation was carried out as described by Woodward and Singh,[14] and the products **4** were fractionally distilled, giving [yield, boiling point, ir ($cm^{-1}$) in $CHCl_3$] **4a**, 10.3%, 93–98° (2 mm), 1650, 1625; **4b**, 6.8%, 99–105° (1 mm), 1670, 1630; **4c**, 5.1%, 102–111° (1 mm), 1665, 1625; **4d**, 2.9%, 107–117° (1 mm), 1660, 1630.

**Rearrangements. A. In Acetic Anhydride.**—A solution of 500 mg of dienone **4** in 50 ml of acetic anhydride containing 3–4 drops of concentrated sulfuric acid was either allowed to stand 24 hr at room temperature or heated at 100° for 30 min. The solution was diluted with water and extracted with ether, and the ether was pumped off after drying over magnesium sulfate. Portions of the weighed residue were chromatographed quantitatively on a Varian Aerograph Model 700 gas chromatograph using a 10-ft (**4a**) or 20-ft (**4b–d**) 10% Carbowax 60/80 Chromosorb W column at 150°.

Total yields were: from **4a**, 72%; **4b**, 85–90%; **4c**, 79–83%; **4d**, 81–91%. Several runs were made in each case. Unrearranged dienone was obtained with **4b–d** and was separated quantitatively in the chromatograph.

**B. In Aqueous Sulfuric Acid.**—A solution of 500 mg of **4** in 5 ml of 20.6 *N* sulfuric acid was kept in a bath at 51.5° for 2 days. Quantitative work-up was as in A. Total yields were: from **4a**, 90%; **4b**, 83%; **4c**, 80–93%; **4d**, 75–89%. Small amounts of unrearranged **4c** and **4d** were obtained in some runs and were separated as in A.

**C. In Concentrated Hydrochloric Acid.**—A solution of 500 mg of **4a** in 5 ml of the acid was either kept at room temperature for 4 days or boiled for 30 min. Work-up and separation were as in A. Total yields were always close to 90%. Two runs at room temperature gave an average of **5a**:**6a** of 15:85. Five runs at reflux gave the same result.

**Product Identification.**—Products **5a**, mp 86–87°, **6a**, mp 103–105°, **7a**, mp 73–74°, and **8a** (liquid) were identified by comparison with data in the literature. Furthermore, **6a** was acetylated to form **8a**, while **7a** and **8a** were hydrolyzed to **5a** and **6a** by boiling in aqueous 20% KOH. Product **8b** (liquid) was identified by comparison with data in the literature.[11] Hydrolysis of **8b** gave **6b** (liquid) which was shown by pmr to be identical with **6b** obtained from rearrangement of **4b** in 20.6 *N* sulfuric acid. The identities of the two other products from **4b** were assumed to be as shown because they were the only other products obtained in the rearrangements (**5b** in 20.6 *N* sulfuric acid, and **7b** in acetic anhydride). Products **6c**, mp 66.5–68.5°, **6d** (liquid), **8c** (liquid), and **8d** (liquid) were identified by comparison of their pmr and infrared spectra with those of **6a**, **6b**, **8a**, and **8b**. The amounts of products **5c**, **5d**, **7c**, and **7d** were too small to allow identification. Identities were assumed since no other products than these and the major ones (**6**, **8**) were observed in the glc chromatograms.

**Pmr of products (aromatic region)** follows: **6a** (d, 6.4, 6.3), **6b** (d, 6.3, 6.2), **6c** (d, 6.4, 6.35), **6d** (d, 6.4, 6.35); $J$ = 3 cps in all cases; **8a** (s, 6.6), **8b** (s, 6.65), **8c** (s, 6.5), **8d** (s, 6.65); **5a** (q, 6.85, 6.40, 6.45, 6.35, $J$ = 8, 8, and 14 cps), **7a** (q, 7.05, 6.90, 6.75, 6.60, $J$ = 9 cps).

**Registry No.**—**4a**, 703-02-6; **4b**, 13984-73-1; **4c**, 34956-90-6; **4d**, 34956-91-7; **5a**, 4242-05-1; **6a**, 3718-79-4; **6b**, 34956-94-0; **6c**, 34956-95-1; **6d**, 34956-96-2; **7a**, 34956-97-3; **8a**, 34956-98-4; **8b**, 34956-99-5; **8c**, 34957-00-1; **8d**, 34957-01-2.

(13) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 337.

(14) R. B. Woodward and T. Singh, *J. Amer. Chem. Soc.*, **72**, 494 (1950).

## An Improved Synthesis of 5-Alkylresorcinols

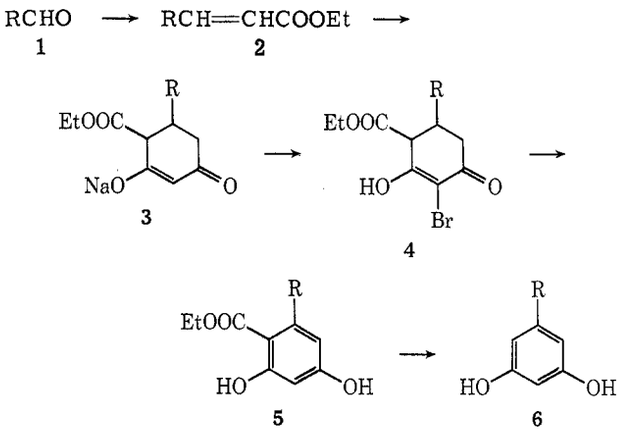
ROBERT S. MARMOR

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

*Received January 4, 1972*

There are at present three general methods for preparing 5-alkylresorcinols;[1-3] however, they are tedious and expensive. I wish to report here an improvement of the last of these methods[3] which should be of convenience to workers requiring 5-alkylresorcinols in pharmaceutical research and, in particular, in the preparation of Cannabis (marijuana) analogs.

The synthetic scheme is outlined as follows.




The aldehyde **1** was converted in high yield to the β-alkylacrylate ester **2** on reaction with the sodium salt of triethyl phosphonoacetate[4] (see Table I). Michael addition of the sodium salt of ethyl acetoacetate to **2** gave **3**. The yield of **3** was dependent on

(1) C. M. Suter and A. W. Weston, *J. Amer. Chem. Soc.*, **61**, 232 (1939). Procedure involves reaction of Grignard reagent with 3,5-dimethoxybenzamide followed by reduction of the ketone product and demethylation. See also applications of their procedure by R. Adams, *et al.*, *ibid.*, **70**, 664 (1948); **71**, 1624 (1949).

(2) J. L. Dever, U. S. Patent 3,278,606 (Monsanto, 1966); *Chem. Abstr.*, **65**, 20062e (1966). Procedure involves conversion of 1,3,5-trichlorobenzene to 1,3-dimethoxy-5-chlorobenzene followed by formation of Grignard reagent, reaction with carbonyl compound, reduction, and demethylation.

(3) (a) R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 311 (1945); (b) F. Korte and H. Sieper, *Justus Liebigs Ann. Chem.*, **630**, 71 (1960); (c) R. Valters and O. Neilands, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, **6**, 710 (1968); *Chem. Abstr.*, **70**, 77495t (1969).

(4) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

TABLE I

RCH=CHCOOEt

| Registry no. | R | Yield RCH=CHCOOEt based on RCHO, % | Bp, °C (mm) |
|---|---|---|---|
| 15790-86-0 | $(CH_3)_2CH$ | 86 | 79–81 (31)[a] |
| 34993-63-0 | $(CH_3)_2CHCH_2$ | 90 | 96 (34–30)[b] |
| 22147-62-2 | $(CH_3)_3C$ | 88 | 92–93 (34)[c] |
| | $CH_3(CH_2)_4$ | 87 | 57–62.5 (1.4)[d] |
| 34993-65-2 | $(CH_3)_3CCH_2$ | 92 | 61 (3.3)[e] |
| | $CH_3(CH_2)_5$ | 89 | 70–75 (0.90)[f] |
| | $CH_3(CH_2)_{10}$ | 82 | 106–110 (0.02)[g] |

[a] Lit.[4] bp 65° (15 mm); nmr for

$(CH_3)_2CHCH{=}CHCOOCH_2CH_3$
a b c d e f

$\delta$ 1.05 (d, 6, $J_{ab}$ = 7 Hz, a), 1.23 (t, 3, $J_{ef}$ = 7 Hz, f), 2.4 (m, 1, b), 4.07 (q, 2, e), 5.63 (d of d, 1, $J_{cd}$ = 16, $J_{bd}$ = 1.5 Hz, d), 6.80 (d of d, 1, $J_{bc}$ = 7 Hz, c). [b] Lit. bp 106–107° (5 mm) (Japanese patent); *Chem. Abstr.*, **54**, 6551*b* (1960) (literature boiling point seems unreasonably high); nmr for

$(CH_3)_2CHCH_2CH{=}CHCOOCH_2CH_3$
a b c d e f g

$\delta$ 0.92 (d, 6, $J_{ab}$ = 6 Hz, a), 1.24 (t, 3, $J_{fg}$ = 7 Hz, g), 1.5–2.2 (m, 3, b + c), 4.10 (q, 2, f), 5.69 (d of t, 1, $J_{de}$ = 16, $J_{ce}$ = 1 Hz, e), 6.84 (d of t, 1, $J_{cd}$ = 7 Hz, d). *Anal.* Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.03; H, 10.39. [c] Lit. bp 54° (12 mm): F. Bohlmann, H. L. Ahrens, and H. Kritzler, *Abh. Braunschweig. Wiss. Ges.*, **9**, 173 (1957); *Chem. Abstr.*, **52**, 10875*a* (1958); nmr for

$(CH_3)_3CCH{=}CHCOOCH_2CH_3$
a b c d e

$\delta$ 1.05 (s, 9, a), 1.24 (t, 3, $J_{de}$ = 7 Hz, e), 4.13 (quartet, 2, d), 5.63 (d of d, 1, $J_{bc}$ = 16 Hz, c), 6.87 (d of d, 1, b). [d] Lit. bp 70–72° (1.5 mm): M. Jacobson, *J. Amer. Chem. Soc.*, **75**, 2584 (1953). [e] Nmr for

$(CH_3)_3CCH_2CH{=}CHCOOCH_2CH_3$
a b c d e f

$\delta$ 0.95 (s, 9, a), 1.25 (t, 3, $J_{ef}$ = 7 Hz, f), 2.05 (d of d, 2, $J_{bc}$ = 8, $J_{bd}$ = 1 Hz, b), 4.13 (q, 2, e), 5.71 (d of t, 1, $J_{cd}$ = 16 Hz, d), 6.88 (d of t, 1, c). *Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.30; H, 10.69. [f] Lit. bp 99.5–102° (5 mm): J. Cason, N. L. Allinger, G. Sumrell, and D. E. Williams, *J. Org. Chem.*, **16**, 1181 (1951). [g] Lit. bp 165–167° (11 mm): L. P. Kyrides, F. B. Zienty, G. W. Steahly, and H. L. Morrill, *J. Org. Chem.*, **12**, 577 (1947).

the steric hindrance presented by the $\beta$-alkyl group of **2** (see Table II). When R = *tert*-butyl, no product had formed after 20 hr, but after 4 weeks some precipitate had formed which did not give rise to 5-*tert*-butylresorcinol. When R = isopropyl, a low yield of the desired product **3** was obtained in 20 hr which gave pure **6** after subsequent steps. Extending the reaction time to 3 days gave more **3** but the **6** obtained from this material was impure (nmr). Yields of **3** were low in the cases R = neopentyl and R = carbethoxymethyl, but were quite good for R = isobutyl and for the linear series R = methyl, *n*-amyl, *n*-hexyl, and *n*-undecyl. The Michael condensation between ethyl tiglate and ethyl acetoacetate did not proceed under these reaction conditions.

Monobromination of **3** to give **4** was accomplished with cupric bromide in 1,2-dimethoxyethane (DME). The published procedures used bromine in acetic acid and obtained ethyl 2,4-dihydroxy-3,5-dibromo-6-alkylbenzoate in fair yields, but poor in the case R = *n*-amyl.[3] Overall yields of **6** from **3** were decreased (30–50% yield in the case R = *n*-amyl) when cupric chloride was substituted for cupric bromide in this step, or when DMF, methanol, or dichloromethane replaced DME as the solvent. In addition, it was necessary to avoid the premature thermal dehydrobromination of **3** during work-up. This decomposition was apparently inhibited by the presence of residual DME. Cuprous bromide was recovered quantitatively.

The unstable bromodione **4** was dehydrobrominated in refluxing DMF to give crude **5**, which presumably underwent partial hydrolysis and decarboxylation to give some **6**. Modest yields of pure **5** were obtained in the cases R = methyl, *n*-undecyl, and carbethoxymethyl where solubility differences made it possible to separate the mixture. A trace of **5**, R = *n*-hexyl, was also isolated. Conversion of crude **5** to **6** was accomplished with aqueous base as per the published procedure.[3] In the case R = carbethoxymethyl, a complex product mixture resulted from which no phenylacetic acid could be isolated. Distillation gave in all cases pure **6** as a pale yellow viscous oil, some of which crystallized (see Table II). Overall yields of **6** from **3** were 75–81%.

## Experimental Section

**General Comments.**—The aldehydes used were purchased from Eastman and Aldrich and were distilled before use with the exception of pivaldehyde and 3,3-dimethylbutyraldehyde, which were prepared by the method of Brown and Tsukamoto.[5] Ethanol was further dried by distillation from calcium ethoxide. 1,2-Dimethoxyethane was distilled from potassium. Cupric bromide was prepared in large scale from cupric oxide and a 5% excess of the calculated amount of concentrated hydrobromic acid, followed by sufficient bromine to remove the milkiness on dilution of a drop of the mixture with water. Concentration gave black cupric bromide which was dried *in vacuo* over potassium hydroxide flakes. Dimethylformamide (B & A) was used as received. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

**Triethyl Phosphonoacetate.**[6]—Ethyl chloroacetate (650 g, 5.3 mol, freshly distilled, bp 143.0–143.5°) and triethyl phosphite [880 g, 5.3 mol, freshly distilled, bp 69° (35 mm)] were thoroughly mixed and placed in a 3-l. flask equipped with an immersed thermometer and condenser, and under an atmosphere of nitrogen. The reaction mixture was heated and stirred and slowly brought to 125°, and then the external heat was discontinued for 30 min as the reaction proceeded. A vigorous but controlled evolution of ethyl chloride occurred. The temperature was then brought to 160° over a 75-min period and held there for 8 hr, after which time ethyl chloride evolution had stopped. The liquid was allowed to cool overnight, and then distilled through a 12-in. Vigreux column, giving, after a small forerun, product at 74–77° (0.03 mm), 1141 g (96%), as a colorless and practically odorless liquid [lit.[6] bp 109° (0.80 mm)].

**Conversion of Aldehyde 1 to Ethyl $\beta$-Alkylacrylate (2).**—In a 3-l. flask equipped with a mechanical stirrer, condenser, and dropping funnel was placed 45.3 g of 53% sodium hydride (dispersion in mineral oil, 1.0 mol) and 1 l. of dry ether. The flask was swept with nitrogen and maintained under positive nitrogen pressure. The reaction mixture was stirred in an ice bath while 224.2 g (1.0 mol) of triethyl phosphonoacetate was added dropwise over 75 min. The mixture then was stirred at reflux for 1 hr, at which time hydrogen evolution had completely stopped. The mixture then was thoroughly cooled in a salted ice bath which was frequently renewed during the course of the addition of the aldehyde (1.0 mol), which was done dropwise over about 1 hr at this scale. The reaction mixture occasionally became viscous near the end of the addition, but redissolved

(5) H. C. Brown and A. Tsukamoto, *J. Amer. Chem. Soc.*, **83**, 4549 (1961).

(6) The procedure using ethyl chloroacetate is recorded here because it is generally believed that the more expensive ethyl bromoacetate is required; see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1216.

TABLE II

| Registry no. | R | Yield of 3 from 2, % | Yield of 6 from 3, % | Bp (mm) or mp, °C, of 6 | Nmr, δ (solvent) of 6 | Carbon calcd (found), % | Hydrogen calcd (found), % |
|---|---|---|---|---|---|---|---|
| 504-15-4 | $CH_3$ | 77 | 75 | 112 (0.06),[a] 96–97 | ($D_2O$) 2.17 (s, 3, Me), 5.0 (broad, 2, HOD), 6.33 (s, 3, aryl) | | |
| 34993-66-3 | $(CH_3)_2CH$ | 22 | 75 | 121 (0.07)[b] | ($CDCl_3$) 1.00 (d, 6, $J$ = 7 Hz, Me), 2.6 (m, 1, CH), 6.30 (s, 3, aryl), 7.3 (broad, 2, OH) | 71.02 (70.55) | 7.95 (7.93) |
| 34993-67-4 | $(CH_3)_2CHCH_2$ | 84 | 79 | 120 (0.04), 94.5–95.0 from hexane | (Acetone-$d_6$) 0.87 (d, 6, $J$ = 7 Hz, Me), 1.7 (m, 1, CH), 2.30 (d, 2, $J$ = 7 Hz, $CH_2$), 6.10 (s, 3, aryl), 8.0 (broad, 2, OH) | 72.26 (72.00) | 8.49 (8.52) |
| 500-66-3 | $CH_3(CH_2)_4$ | 76 | 80 | 132 (0.05),[c] 44–46 | ($CDCl_3$) 0.7–1.8 (m with max at 0.82 and 1.27, 9), 2.4 (broad, 2, $CH_2$), 6.28 (s, 3, aryl), 7.25 (s, 2, OH) | 73.30 (72.98) | 8.95 (9.14) |
| 34993-68-5 | $(CH_3)_3CCH_2$ | 30 | 78 | 129 (0.05)[d] | ($CDCl_3$) 0.81 (s, 9), 2.27 (s, 2, $CH_2$), 6.23 (s, 3, aryl), 6.4 (broad, 2, OH) | 73.30 (72.81) | 8.95 (8.91) |
| 5465-20-3 | $CH_3(CH_2)_5$ | 76 | 81 | 142 (0.05)[e] | ($CDCl_3$) 0.7–1.8 (m with max at 0.82 and 1.23, 11), 2.3 (broad, 2, $CH_2$), 6.23 (s, 3, aryl), 7.05 (s, 2, OH) | 74.19 (74.10) | 9.34 (9.36) |
| 34155-91-4 | $CH_3(CH_2)_{10}$ | 85 | 78 | 173 (0.03),[f] 75–76 from hexane | ($CDCl_3$) 0.7–1.7 (m with max at 1.27), 2.4 (broad, 2, $CH_2$), 6.2 (broad, 2, OH), 6.27 (s, 3, aryl) | 77.22 (76.99) | 10.67 (10.64) |
| | $EtOOCCH_2$ | 31 | | | | | |

[a] Lit. mp 106–108°, bp 147° (5 mm), ref 3a. Melting point of product was unchanged after repeated recrystallization and distillation; however, when seeded while molten with authentic orcinol, product then had mp and mmp 106–108°. [b] Product did not crystallize: lit. mp 110°, bp 120° (0.15 mm); J. P. Brown, D. H. Johnson, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 2019 (1951). [c] Lit. mp 49° (ref 3a), bp 162–164° (5 mm) (ref 1). [d] Product did not crystallize, but formed a hydrate on recrystallization from water, mp 116–117°. [e] Lit.[1] bp 192–195° (11 mm). [f] Lit. mp 67–71°: M. Asano and K. Yamaguti, *J. Pharm. Soc. Jap.*, 60, 105 (1940); *Chem. Abstr.*, **34**, 5070 (1940).

on continued stirring. The cold mixture was stirred for an additional 10 min, and then was slowly brought to reflux, whereupon a heavy, viscous, oily precipitate of sodium diethyl phosphate separated, rendering further stirring impossible. The reaction mixture was refluxed for 10 min, and then the clear ether layer was decanted from the oil. The remaining oil was dissolved in 500 ml of warm water and the upper organic layer was separated. The aqueous layer was extracted with 200 ml of ether. The combined organic solutions were extracted with 200 ml of saturated sodium bicarbonate solution, dried with magnesium sulfate, filtered, rotary evaporated, and distilled through a Vigreux column. The products were all colorless liquids which gave ir absorptions at 1655 and 1720 $cm^{-1}$ and had nmr spectra which suggested that they were pure trans isomers. See Table I for specific yields, boiling points, and nmr spectra.

**Condensation of Ethyl β-Alkylacrylate with Ethyl Acetoacetate.**—A solution of sodium ethoxide was prepared from 25.3 g (1.1 g-atom) of sodium and 500 ml of dry ethanol in a 2-l. flask equipped with a mechanical stirrer, condenser, and dropping funnel, and under positive nitrogen pressure. To the solution was added 156 g (1.2 mol) of ethyl acetoacetate. The solution was stirred at reflux for 30 min, and then the desired ethyl β-alkylacrylate **2** (1.0 mol) was added dropwise to the refluxing solution over approximately 90 min. The dione sodium salt **3** began to precipitate at or near the end of the addition in the case of the less hindered ethyl β-alkylacrylates, whereas several hours after the addition were required for the more hindered esters. The reaction mixtures were in any case refluxed for about 20 hr, cooled in ice, and filtered. The precipitate was washed with 500 ml of ice-cold absolute ethanol, followed by several portions of ether, then air-dried for 1 hr. The white, powdery product was placed for 1 hr in a 90° oven, then dried overnight *in vacuo*. No difference in yield was observed in the following steps whether the product was used immediately or had been stored for several months at room temperature. See Table II for specific yields.

**5-Alkylresorcinol** (**6**).—In a 250-ml flask equipped with a powerful magnetic stirring assembly and a condenser were placed the desired dione sodium salt **3** (100 mmol) and 100 ml of DME. The system was flushed with nitrogen and stirred at room temperature while 44.67 g (200 mmol) of cupric bromide was added portionwise over 5 min under a stream of nitrogen. The solution became warm and stirring was continued without external heating for 30 min, and then the solution was stirred for 1 hr at reflux. The solution was cooled and rotary evaporated while care was taken not to heat the warming bath above 50°, and not to remove more than approximately 65 ml of the DME. The remaining solution was diluted with 200 ml of benzene and filtered to remove the mixture of cuprous and sodium bromides. The precipitate was washed with 50 ml of benzene and dried, giving a quantitative yield of inorganic salts. Washing with water and redrying gave a quantitative yield of white cuprous bromide. The combined benzene filtrates were rotary evaporated (50° maximum warming bath) and the crude bromodione was taken up in 100 ml of DMF and placed in a 500-ml flask under nitrogen. The solution was stirred and brought to reflux (the temperature must be raised fairly slowly in larger scale runs to avoid a sudden exotherm). Low boilers were allowed to escape until the liquid temperature reached 150°, and then the mixture was refluxed for 4 hr, allowed to cool, poured into 500 ml of water, and extracted with three 100-ml portions of dichloromethane. (In the orcinol preparation, R = methyl, the DMF solution was not diluted with water but instead the DMF was removed on the rotary evaporator under 1.0 mm vacuum, 90° warming bath.) The combined dichloromethane layers were dried with magnesium sulfate, filtered, and rotary evaporated. The residue then was either converted to the 5-alkylresorcinol **6**, as will be described next, or purified to give ethyl 6-alkyl-2,4-dihydroxybenzoate (**5**). To this residue was added a solution of 24 g (600 ml) of sodium hydroxide in 200 ml of water. The mixture was stirred at reflux under nitrogen in the hood (some dimethylamine evolution) for 3 hr, and then cooled in ice and acidified cautiously (some frothing may occur) with a cold solution of 20 ml (720 mmol) of concentrated sulfuric acid in 80 ml of water while stirring under nitrogen in an ice bath. The solution was then brought to reflux under nitrogen for 5 min, cooled, and extracted with several portions of ether. The combined ether layers were dried with magnesium sulfate, filtered, and rotary evaporated. The crude product, a black, viscous oil, was distilled (short path, air cooling) and product was collected in all cases as a pale yellow, viscous oil. See Table II for yields and physical data.

**Ethyl 6-Methyl-2,4-dihydroxybenzoate (Ethyl Orsellinate).**—The above residue (R = methyl) remaining after DMF removal *in vacuo* was treated with 100 ml of water which dissolved the orcinol and precipitated the ethyl orsellinate. The mixture was filtered and the precipitate was dissolved in 150 ml of hot chloroform. This solution was dried with sodium sulfate, filtered, and diluted with 150 ml of hot hexane. On standing, most of the colored material came out as an oil. The yellow, supernatant liquid was decanted from the oil and boiled down to a volume of 150 ml. On slow cooling, the product separated as pale yellow crystals, 8.2 g (42%), mp 127.5–9.5°. Two recrystallizations from 50% aqueous ethanol, using activated charcoal, gave a pure white product, mp 131.0–131.5° (lit.[3c] mp 130.0–131.5°).

**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 ($CCl_4$) $\tau$ 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).