2-one followed by conversion to the chloride. In this case, a ca. 1:2 mixture of the 1-methyl and 2-methyl compounds were formed.

Carbocation Preparations. These were prepared at ca. −120 °C by using previously described procedures.[19]

NMR Spectra. ^1H spectra of A–B and the 2-methyl analogue were obtained on a Varian XL-200 spectrometer, either locked ($Me_4Si/(CD_3)_2O$) or unlocked). Peaks were referenced internally to the H-4 proton (this peak is inexplicably a 4-Hz doublet with good resolution). ^1H spectra of A′–B′ were obtained unlocked on a Bruker AM-500 instrument. ^2H spectra of the 2-methyl-d_1 cation were obtained unlocked at 30.7 MHz on the XL-200, while ^2H spectra of A′–B′ were obtained at 76.8 MHz on the Bruker instrument. These latter spectra were internally referenced to the 4-^2H peak, this assumed to be the same as that of the corresponding proton compound.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for generous financial support. We also thank Bruker Canada for the use of the 500-MHz NMR instrument and Professor R. Childs of McMaster University for laboratory facilities.

Registry No. C, 92314-77-7; C′, 92314-78-8; h_1d_{10} cation, 92456-12-7; $h_{10}d_1$ cation, 92456-13-8; D_2, 7782-39-0; 2-norbornyl cation, 24321-81-1; 2-methyl-2-norbornyl cation, 3197-78-2; *exo*-2-chlorobicyclo[2.2.1]heptane-1,3,3,4,5,5,6,6,7,7-d_{10}, 92314-79-9; *exo*-2-chloro-*endo*-2-methyl-d_3-bicyclo[2.2.1]heptane-3,3,4,5,5,6,6,7,7-d_9, 92314-80-2.

(19) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.

Malonic Ester Derivatives. 2[1]

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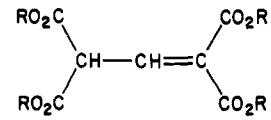
The reactivity, ready availability, and low cost of malonic esters combine to make them attractive starting materials in many synthetic schemes. This paper continues some initial investigations originally designed to produce precursors to dodecahedrane; in the work reported here, methyl esters were used rather than ethyl esters because melting points are generally higher.[4,12]

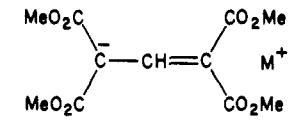
This paper furnishes data on the pK_a of **1a**, the alkylation of its sodium and tetra-*n*-butylammonium salts **2b** and **2a** by methyl bromoacetate, and an attempted Michael reaction on the alkylation product **3**: this last reaction produced an unexpected result.

Indications that **1a** might be unusually acidic may be gleaned from the fact that its sodium salt is both stable to water and recoverable in good yield after crystallization from suitable alcohols.[5] Acetic acid is strong enough to convert **2b** to **1a**, and sodium bicarbonate is basic enough for the reverse process.[6] The parent ester **1a** is easily purified as a solid, mp 50–51 °C[12] (the ethyl ester **1b** is a liquid at room temperature), and it may be titrated with sodium hydroxide or with tetraalkylammonium hydroxide[7] in methanol–water mixtures to give the corresponding salts. A determination of the pK_a of **1** does not appear to have been reported: we were pleasantly surprised to find a pH of 5.8 for the half-neutralization point in a titration of **1a** with tetra-*n*-butylammonium hydroxide solution. Similar titration of **1a** with sodium hydroxide solution showed a pH at half-neutralization of 5.6, in a medium containing a greater proportion of water to methanol.[10b] The sodium salt **2b** has been known for about a hundred years,[8] but the tetraalkylammonium salts have not been previously described.[16]

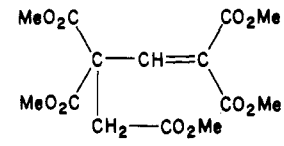
The alkylation[9] of salts of **1a** by methyl bromoacetate proceeded smoothly, once suitable conditions had been established (see Experimental Section); the optimum yield of **3** was 94%.



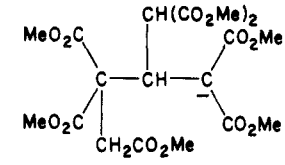
1a, R = Me
1b, R = Et



2a, M = $N(CH_2CH_2CH_2CH_3)_4$
2b, M = Na



3



4

An attempted Michael reaction on **3** by the sodio derivative of dimethyl malonate in methanol did not yield the expected **4**; an immediate yellow color in the system (an indication of formation of the sodium salt **2b**) suggested that a substitution had occurred (eq 1).

Triester **5** was identified by NMR analysis and by comparison with an authentic sample; acidification of the nonneutral fraction from the reaction furnished **1a**.

(1) Part 1 of this series is considered to be the paper by Galakatos et al. (Galakatos, N. G.; Hancock, J. E. H.; Morgan, O. M.; Roberts, M. R.; Wallace, J. K. *Synthesis* **1978**, 472.

(2) From the B.A. Thesis of Andrew Alex Chiu, Reed College, May 1983.

(3) Research assistant, (a) summer 1980; (b) summer 1979.

(4) That a methyl ester of a given acid has a melting point higher than that of the corresponding ethyl ester is exemplified by data in several sources: see, for example: (a) Palomaa, M. H.; Mikkilä, I. *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 1659. (b) [The experimental section of] Crombie, L.; Hancock, J. E. H.; Linstead, R. P. *J. Chem. Soc.* **1953**, 3496. (c) Reference 12 and similar entries in "Beilstein".

(5) See, for example: ref 1 and literature cited therein.

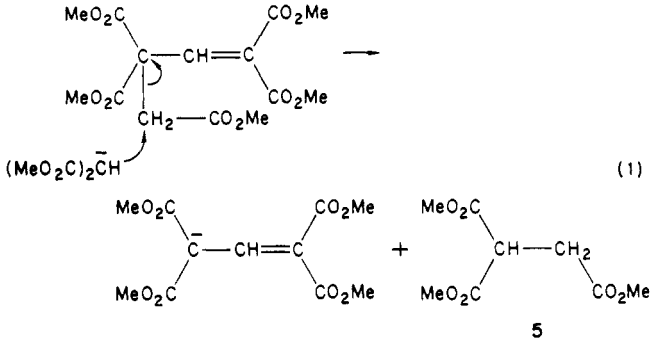
(6) Compare: Bateman, L.; Koch, H. P. *J. Chem. Soc.* **1945**, 221. Sodium bicarbonate and sodium carbonate are unsatisfactory because they are soluble in water but insoluble in methanol; **1a** has the reverse solubility properties. An initial reluctance to use hydroxide bases because of possible hydrolysis proved groundless.

(7) Preliminary work by M. Bossé (summer research assistant, 1980) with tetraalkylammonium salts of **1b** suggested that the tetra-*n*-butylammonium salt would be the optimum choice. We were interested in such salts because of anticipated greater solubilities in organic solvents, compared to the sodium salts such as **2b**, which is sparingly soluble in cold common organic solvents. Salt **2a** is very soluble in cold acetonitrile and is easily crystallized from ethyl acetate.

(8) See ref 1 and literature cited therein.

(9) Few alkylations of salts of **1** appear in the literature; indeed, alkylations of only the sodium salt of **1b** have been reported. (a) Methylation: the highest yields in a methylation appear to be those obtained by F. B. Thole and J. F. Thorpe (*J. Chem. Soc.* **1911**, *99*, 2196), who obtained a yield of 83% with methyl iodide in ethanol on the steam bath for 5 h. Earlier workers (ref 13) had conducted their experiments at 150–160 °C in sealed tubes and reported that the presence of ethanol led to unsatisfactory results under those conditions. (b) Ethylation. (i) With ethyl iodide in 80% yield: Thole, F. B.; Thorpe, J. F. *J. Chem. Soc.* **1911**, *99*, 2196. (ii) With ethyl iodide in 53% yield; Lukeš, R.; Heřmánková, V.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1959**, *24*, 1699. (c) Propylation. (i) With 1-iodopropane in 50% yield; see Lukeš et al. (ii) With 2-bromopropane (ref 14) and 2-iodopropane (ref 15) the reaction furnished triethyl trimesate, and much gas, thought to be propene. (d) Butylation with 1-bromobutane in 30% yield, see Lukeš et al. These alkylations are generally not reported in "Beilstein" under reactions of propene-1,1,3,3-tetracarboxylic esters or of its salts; they were found by a thorough search of "Beilstein" in the complete section on monounsaturated tetracarboxylic esters.

0022-3263/84/1949-4313$01.50/0



(1)

5

The pK_a of dimethyl malonate is approximately 13;[10a] the degree of increased acidity of **1a** is surprising, but several variables must be taken into account in such comparisons. Although it is tempting to ascribe the increased acidity to the increased resonance stabilization in the anion, there may be effects due to entropy of solvation which can only be uncovered by further data.

The notion that a leaving group in a nucleophilic displacement may be derived from a malonic ester anion seems foreign to classical organic chemistry, yet the result described here may be so viewed; it is rationalized on the basis of the difference of pK_a between **1a** and the parent acid of the product **4** originally desired. This parent would presumably have exhibited a pK_a not very different from 13. Since Michael reactions are reversible, the reaction in this case proceeded via a pathway providing the anion of the stronger acid. The notion that good leaving groups which bear a negative charge are salts of strong acids seems well established.[11] Finally, molecular models show that approach of the anion of **6** to the methine unit in **3** is considerably hindered; by contrast, the α methylene unit in **3** is much more open to such an attack.

$CH_2(CO_2CH_3)_2$
6

Experimental Section

All melting points are uncorrected. IR spectra were taken with a Perkin-Elmer Model 599 spectrophotometer, and ^1H NMR spectra with a Hitachi-Perkin-Elmer Model R20B instrument. Combustion analyses were performed by Galbraith Laboratories, Inc. Only the major absorption peaks (IR) are reported.

Tetramethyl Sodiopropene-1,1,3,3-tetracarboxylate (2b). The general procedure was adapted from that of ref 1. CAUTION: the reaction may evolve carbon monoxide.[1]

The chloroform used below was purified from its ethanol preservative by washing 3 times with deionized water and drying the resultant liquid over anhydrous magnesium sulfate prior to use to avoid possible problems of ester interchange.

A 5-L, three-necked flask was equipped with a heavy-duty stirrer and a Friedrichs condenser protected by a drying tube. The third neck was stoppered. Methanol (reagent grade, 3 L) was added, and the system was cooled in ice–water. Freshly cut sodium (138 g, 6.0 mol) was gradually added to the rapidly stirred methanol solution. During the very exothermic reaction, the drying tube was removed and replaced by a hose leading to an open window. After all the sodium had dissolved, the drying tube was replaced, and the mixture allowed to cool to 30–35 °C. The stopper in the third neck was replaced by a 500-mL pressure-compensated addition funnel, through which dimethyl malonate (Aldrich, 396 g, 3.0 mol) was added. A thick precipitate occurred in some runs (compare the behavior experienced in the ethyl ester series, see ref 1). The chloroform (see above, 240 g, 2.0 mols) was added dropwise, whereupon the system gradually became yellow and deposited a precipitate. The mixture was stirred overnight at room temperature and then heated to reflux for 2 h. The initial bright yellow color became intense orange; very little heat was necessary to achieve reflux—evidently an exothermic process took place (after the first hour of heating, the heating mantle was removed, yet the mixture continued to boil for over 15 min). The mixture was allowed to cool to room temperature and placed in a cold room at 6 °C overnight.

Filtration of the mixture under suction and rinsing the precipitate with cold methanol (3 × 50 mL) gave sodium chloride (237 g, 90%). The filtrate was reduced in volume to about 2 L via vacuum evaporation and then cooled to −14 °C overnight. Yellow crystals of **2b** were filtered under suction (175.6 g, 39.5%, mp 263.0–264.5 °C)[18] and the filtrate again placed on the rotary evaporator, eventually yielding a second impure crop, in the form of a moist orange solid (275.0 g, 61.9%). These two crops were individually converted to the parent acid.

Conversion of 2b to 1a. (a) The yellow salt of the first crop (above) was dissolved in deionized water (850 mL) and gradually acidified with 6 M hydrochloric acid (ca. 100 mL) in a 2-L separatory funnel, with careful check of the pH from time to time. The mixture became cloudy, a white precipitate formed, and the yellow color disappeared. Extraction with methylene chloride (2 × 250 mL, then 8 × 100 mL) washing these extracts with saturated sodium chloride solution, drying ($MgSO_4$), and evaporation in vacuo gave a clear, colorless viscous oil which crystallized after seeding. The crude product weighed 134.8 g, mp 47–51 °C (83% conversion yield from the salt).

(b) The second crop of sodium salt was processed in deionized water (1500 mL) but it was necessary to filter the solution to remove insoluble impurities. Acidification and extraction as above gave a tan-colored syrup which only partly crystallized on cooling and seeding (188.5 g). The combined yield of crude **1a** was 323.3 g (78.6%).

The crude products were crystallized from diethyl ether–*n*-hexane. It was necessary to crystallize the second crop twice, with hot filtration. The final overall yield of **1a** was 218 g (53%): mp 49–50.5 °C; NMR (CCl_4) δ 3.73 (s), 3.77 (s), 4.55 (d, J = 11 Hz), 6.98 (d, J = 11 Hz); Shoppee and Hughes[19] reported NMR ($CDCl_3$) δ 3.78 (s), 3.82 (s), 4.72 (d, J = 9.5 Hz), 7.22 (d, J = 9.5 Hz); IR (KBr) 2960, 1740 (br), 1438, 1368, 1250 (br, vs), 1155, 1125, 1068, 330 cm^{-1}.

Preparation of Salt 2a. The parent acid **1a** (6.45 g, 0.0239 mol) was dissolved in methanol (70 mL), and deionized water (16 mL) was added. The pH was monitored (Altex Model 3500 digital pH meter, calibrated at pH 4.01, 7.00, and 10.00 using aqueous

(10) (a) See, for example: Appendix IV to "Introduction to Organic Chemistry", 2nd ed.; Streitwieser, A., Heathcock, C. H., Eds.; Macmillan: New York, 1981. The pK_a quoted is 13.3 for diethyl malonate. (b) That a change of the relative amount of water in the ionizing medium can exert a large effect on the pK_a of an acid is well documented. See, for example: (i) King, J. F. In "Technique of Organic Chemistry"; Weissberger, A., Ed., Interscience: New York, 1963; Vol. XI, Bentley, K. W., Ed., p 323. (ii) "Techniques of Chemistry"; Weissberger, A., Ed.; Wiley-Interscience: New York, 1972; Vol. IV, Part I, 2nd ed., Bentley, K. W., Kirby, G. W., p 630.

(11) See, for example: "Mechanism and Theory in Organic Chemistry", 2nd ed.; Lowry, T. H., Richardson, K. S., Eds.; Harper and Row: New York, 1981; p 339.

(12) For literature, see: "Beilsteins Handbuch der Organischen Chemie", 4th ed.; Richter, F., Ed.; Springer: Berlin, 1961; Third Supplement, Vol. 2, p 2093. It is evident that material prepared in 1936 by Ingold, Parekh, and Shoppee[17] must have been impure; they quote a mp of 43 °C and a mp of 243–249 °C for the sodium salt. See also ref 18.

(13) Compare: Ruhemann, S. *J. Chem. Soc.* **1893**, *63*, 880.

(14) Klemo, G. R.; Welch, K. N. *J. Chem. Soc.* **1928**, 2625.

(15) Hariharan, K. V.; Menon, K. N.; Simonsen, J. L. *J. Chem. Soc.* **1928**, 434.

(16) Although "Beilstein" does not list all the salts which have been characterized, a careful search in the references which it provides led to the following: (a) The guanidinium salt of **1b**, mp 163 °C dec (Ruhemann, S.; Orton, K. J. P. *J. Chem. Soc.* **1895**, *67*, 1008). (b) The diethylamine salt of **1b**, mp 130 °C dec (Ruhemann, S.; Hemmy, A. S. *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 2022). (c) The piperidine salt of **1b** is discussed (but not analyzed) by S. Ruhemann and A. S. Hemmy (ref 16b). (d) Treatment of **1b** with concentrated aqueous ammonia gave a gelatinous yellow precipitate "which is, no doubt the ammonium compound of the ethereal salt"—Ruhemann, S.; Morrell, R. S. *J. Chem. Soc.* **1891**, *59*, 746.

(17) Ingold, C. K.; Parekh, M. M.; Shoppee, C. W. *J. Chem. Soc.* **1936**, 142.

(18) Various melting points have been reported in the literature, with no explanation for the considerable discrepancies: 247–249 °C (ref 17); 270–272 °C (ref 19); 264 °C (ref 20). Compare a similar state of affairs in the ethyl ester series, mentioned in ref 1.

(19) Shoppee, C. W.; Hughes, N. W. *J. Chem. Soc. C* **1971**, 3673.

buffer solutions) as titration was carried out with an aqueous solution of tetra-*n*-butylammonium hydroxide (Fischer Scientific Co., 0.40 ± 0.02 M). The pH at neutralization was 9.5 ($MeOH/H_2O$ (2/1) by volume), and at half-neutralization it was 5.72 (14/5 by volume). Rotary evaporation at water pump pressure gave a residue which was dried by addition of toluene (Burdick and Jackson, 150 mL) and further reduced-pressure evaporation. The resulting yellow solid was dissolved in ethyl acetate (200 mL), filtered, and cooled to −14 °C overnight. Yellow crystals were removed by suction filtration and allowed to dry in air (11.19 g, 91%, mp 110.5–112 °C). An analytical sample was prepared via a second recrystallization from ethyl acetate, followed by drying at 56 °C (0.2 torr for 24 h: mp 111.5–112 °C; NMR ($CDCl_3$) δ 0.95 (s), 1.05 (s), 1.2–1.8 (br m), 3.46 (s), 8.15 (s); IR (KBr) 2960, 1730, 1695, 1648, 1549, 1539, 1435, 1368, 1307, 1240, 1184, 1145, 1080 (vs), 969 cm^{-1}. Anal. Calcd for $C_{27}H_{49}NO_8$: C, 62.87; H, 9.60; N, 2.72. Found: C, 62.70; H, 9.55; N, 2.66.

Preparation of Salt 2b from 1a. Titration of **1a** (5.0 g, 0.0182 mol) in methanol (50 mL) and deionized water (13 mL) with aqueous sodium hydroxide (0.49 M) gave an equivalence point at pH 9.5 and a half-neutralization point at pH 5.6. At the equivalence point the methanol:water ratio was 1:1 by volume, and at the half-neutralization point the ratio was 5:3. Workup by rotary evaporation and recrystallization from methanol (hot filtration) gave sodium salt **2b** in 89% yield (4.80 g): mp 263–265 °C;[18] IR (KBr) 1680 (br), 1640 (br), 1545 (br), 1435, 1250, 1175 (br, vs), 1090 (br) cm^{-1}.

Pentamethyl 1-Butene-1,1,3,3,4-pentacarboxylate (3). This run represents the optimum of six trials, using various techniques. Methyl bromoacetate (1.13 g, 0.0067 mol) and acetonitrile (Burdick and Jackson, 150 mL) were added to a 250-mL round-bottomed flask which was connected to a Soxhlet apparatus. Sodium salt **2b** (2.0 g, 0.0067 mol) was added to the Soxhlet thimble, and the liquid was heated to reflux. After 1 day of reflux, all the salt had been extracted; heating was continued for a further 48 h, and the system was allowed to cool, furnishing a clear yellow solution with a white precipitate. Filtration (suction), and evaporation of the filtrate in vacuo, gave a dark orange residue which was extracted with anhydrous ether (12 mL) and the extract was concentrated in vacuo to give a second orange residue. Bulb-to-bulb distillation (130–150 °C oven temperature/10^{-3} torr) gave 2.20 g (94%) of pentamethyl ester **3** which crystallized on seeding: mp 59–60 °C; NMR (CCl_4) δ 3.12 (s), 3.51 (s), 3.58 (distorted s), 3.67 (s), 7.44 (s); IR (neat) 2990, 1740 (vs), 1378, 1348, 1240 (vs), 1100, 1080, 1132 (vs) cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_{10}$: C, 48.56; H, 5.24. Found: C, 48.80; H, 5.04.

Various other conditions were investigated for synthesis of this pentaester. Alkylation of the tetra-*n*-butylammonium salt **2a** in glyme or in acetonitrile with heating gave a product showing an impurity in the NMR spectrum at 1.5 ppm. Reaction of the same salt in acetonitrile at room temperature for 5–7 days, sometimes with 10–15% excess methyl bromoacetate, gave the ester **3** without the above impurity, but in lower yield. The sodium salt **2b** is so sparingly soluble in glyme that the Soxhlet extraction technique failed completely. Doubling the scale of operation in the detailed synthesis described above, but with 10% excess methyl bromoacetate, furnished the pentaester in 89% yield.

It was difficult to obtain the initial seeds of this new compound: the usual methods involving cooling and scratching proved ineffective. The first crystals appeared on concentration in vacuo of the carbon tetrachloride solution used for obtaining the NMR spectrum.

Attempted Michael Condensation on Ester 3. Preliminary studies with dimethyl malonate in methanol, employing catalytic amounts (ca. 5%) of sodium methoxide, indicated that molar amounts of base would be necessary in order for products to be isolated.

Sodium (0.069 g, 0.0029 mol) was added to methanol (Burdick and Jackson, 10 mL), and when the sodium had dissolved, dimethyl malonate (Aldrich, 1.91 g, 0.0145 mol, 400% excess) was added, followed by pentamethyl 1-butene-1,1,3,3,4-pentacarboxylate (1.0 g, 0.0029 mol). The mixture immediately became bright yellow-green and was allowed to stand at room temperature for 5 days. Evaporation of the methanol at water pump pressure gave a somewhat viscous orange-green residue, which upon evacuation at 10^{-3} torr (room temperature) yielded dimethyl malonate (1.39 g) in a trap cooled with dry ice/Dowanol. The remaining viscous yellow residue was extracted with methylene chloride and water, and upon evaporation of the organic phase from the dried extract, and bulb-to-bulb distillation of the resulting residue at 10^{-3} torr, two fractions were obtained: (1) bp 50–80 °C (0.35 g, 59%) and (2) bp 80–150 °C (0.2 g). NMR analysis and comparison with an authentic sample identified the main component of this neutral fraction as trimethyl ethane-1,1,2-tricarboxylate: NMR (CCl_4) δ 2.70 (d, J = 7 Hz), 3.52 (distorted s), 3.57 (distorted s). The yellow aqueous phase from the above workup was acidified with 6 M hydrochloric acid, whereupon it turned cloudy white. Extraction with methylene chloride (3 × 5 mL), drying ($MgSO_4$), and evaporation in vacuo gave 0.49 g (62%) of ester **1a**, identified by NMR analysis.

Preparation of Trimethyl Ethane-1,1,2-tricarboxylate (5). (With Mr. Ying Ki Kwong). Sodium hydride (3.53 g, 0.15 mol) was covered with glyme (100 mL) in a nitrogen-flushed 250-mL, round-bottomed flask, and the contents were stirred magnetically. Under ice cooling, dimethyl malonate (19.4 g, 0.15 mol) was slowly added. The mixture was allowed to warm to room temperature, and methyl bromoacetate (freshly distilled, 22.77 g, 0.15 mol) was added dropwise; an exothermic reaction occurred and a white precipitate formed. After addition of the methyl bromoacetate was complete, the mixture was stirred for 1 h at room temperature, followed by 1 h at reflux temperature. The cooled mixture reacted neutral to pH paper; it was filtered, the filtrate concentrated on a rotary evaporator at 20 torr, and the residue distilled at 0.02 torr. Three fractions were obtained: (1) bp 25–45 °C (positive sodium fusion test for bromine); (2) bp 81 °C, mp 31–32 °C[21] (14.9 g, 50% of the triester), and (3) bp 110 °C, consisting of the disubstitution product, tetramethyl propane-1,2,2,3-tetracarboxylate (identified by NMR analysis). The NMR spectrum of fraction 2 matched that of the neutral material isolated above from the attempted Michael condensation.

Acknowledgment. We thank Professor Keith Howard for discussion of this material.

Registry No. **1a**, 34456-05-8; **2a**, 92078-62-1; **2b**, 92078-60-9; **3**, 92078-63-2; **5**, 40967-67-7; dimethyl malonate, 108-59-8; chloroform, 67-66-3; methyl bromoacetate, 96-32-2; tetrabutylammonium hydroxide, 2052-49-5; tetramethyl 1,2,2,3-propanetetracarboxylate, 53046-85-8.

(20) Bateman, L.; Jeffery, G. A. *J. Chem. Soc.* **1945**, 211. See also: Bateman, L.; Koch, H. P. *J. Chem. Soc.* **1945**, 216.
(21) Lit. mp 34.5 °C; see Bischoff, C. A. *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 966.

A Straightforward Synthesis of (2*R*)-4-(Benzyloxy)-2-methyl-1-butanol from (*S*)-Citronellol

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Dolichol (**1**), a natural polyisoprenol, controls a glycoprotein synthesis important for maintaining the lives of organisms.[1] A practical and promising synthesis of **1** would be by coupling the naturally occurring polyisoprenol **2** with a Grignard reagent from a chiral C_5 unit **3b** (Scheme I).[2] An important problem to be solved for the manu-

(1) (a) Burgos, J.; Hemming, F. W.; Pennock, J. F.; Morton, R. A. *Biochem. J.* **1963**, *88*, 470. (b) Carroll, K. K.; Vilim, A.; Woods, M. C. *Lipids* **1973**, *8*, 246. (c) Adair, W. L., Jr.; Robertson, S. *Biochem. J.* **1980**, *189*, 441. (d) Tavares, I. A.; Coolbear, T.; Hemming, F. W. *Arch. Biochem. Biophys.* **1981**, *207*, 427.
(2) Suzuki, S.; Mori, F.; Takigawa, T.; Ibata, K.; Ninagawa, Y.; Nishida, T.; Mizuno, M.; Tanaka, Y. *Tetrahedron Lett.* **1983**, *24*, 5103.

0022-3263/84/1949-4315$01.50/0