Experimental Section

The nmr spectra were determined on a Varian A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Diethyl 1-alkynylphosphonates were prepared by our method described earlier[3] and were redistilled before use.

Preparation of Diethyl β-Ketophosphonates 3a–i.—The diethyl 1-alkynylphosphonate 1 (0.025 mol) was refluxed for 3–5 days with a 10–12 molar excess of *n*-butylamine.[4] The excess amine was evaporated at aspirator pressure. The resulting adduct was dissolved in ether (100 ml), and 100 ml of 1% aqueous solution of oxalic acid was added. The two-layer reaction mixture was stirred for 7–8 hr at room temperature and then transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted twice with 25-ml portions of ether. The combined ether extracts were washed with dilute sodium bicarbonate solution, dried ($MgSO_4$), and filtered and ether was distilled off. The resulting oil was short path distilled under reduced pressure.

Acknowledgment.—We wish to acknowledge the National Institutes of Health for support of this work under Grant GM-16828 and the National Science Foundation under Grant GP-10739 We also wish to thank Hoffmann-La Roche, Inc., Nutley, N. J., for their unrestricted grant which helped us to complete this work.

Registry No.—**1a**, 3450-64-4; **1b**, 3450-66-6; **1c**, 40601-31-8; **1d**, 40601-32-9; **1e**, 30238-21-2; **1f**, 30238-20-1; **1g**, 3450-67-7; **1h**, 30238-19-8; **1i**, 40601-37-4; **3a**, 3450-65-5; **3b**, 3452-99-1; **3c**, 40601-40-9; **3d**, 40601-41-0; **3e**, 40601-42-1; **3f**, 40601-43-2; **3g**, 3453-00-7; **3h**, 40601-45-4; **3i**, 40601-46-5.

Dianions of β-Keto Phosphonates. A Two-Step Synthesis of (±)-*ar*-Turmerone

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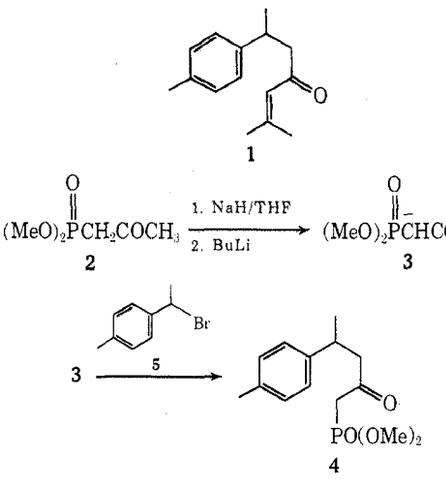
Received March 12, 1973

The monocyclic aromatic sesquiterpene (±)-*ar*-turmerone (**1**) is the chief component of the essential oil from the rhizomes of *Curcuma Longa* Linn.[1] Although the structure of **1** has been confirmed by a number of syntheses,[2] we would like to describe a two-step synthesis of turmerone employing the recently reported method of specifically alkylating a β-keto phosphonate ester at the γ carbon atom.[3]

The alkylation of dianion **3** [prepared by treatment of dimethyl 2-oxopropylphosphonate (**2**) with sodium hydride in anhydrous tetrahydrofuran followed by subsequent metalation with *n*-butyllithium] with *p*-(1-bromoethyl)toluene (**5**) affords the γ-alkylated β-keto phosphonate **4** in 50% isolated yield after purification. The synthesis of β-keto phosphonates (*e.g.*, **4**) *via* the dianion procedure complements the existing methods: Michaelis–Arbusov[4] reaction of trimethyl phosphite with an α-halo ketone and the reaction of dimethyl



α-lithiomethanephosphonate with an ester.[5] We believe that the present method offers some obvious advantages over the existing methods.

Finally, treatment of β-keto phosphonate **4** with sodium hydride in anhydrous dimethoxyethane followed by addition of an excess of acetone affords after 14 hr at 55° a 52% isolated yield of (±)-*ar*-turmerone after purification. The synthetic material exhibits nmr, ir, and mass spectral data in agreement with the previously published data.[2c] The synthesis of **1**, despite its low overall yield, represents the shortest and most convenient route in comparison with previously reported syntheses.

Experimental Section[6]

Preparation of β-Keto Phosphonate 4.—To a suspension of 204 mg (4.8 mmol) of sodium hydride (57%, washed with hexane to remove mineral oil) in 10 ml of freshly distilled tetrahydrofuran under an atmosphere of nitrogen was added dropwise 663 mg (4.0 mmol) of dimethyl 2-oxopropylphosphonate (**2**)[7] in 1.5 ml of dry THF. The resulting slurry was stirred at room temperature for 2 hr to allow for complete formation of the sodio derivative of **2**. The reaction mixture was then cooled to 0° and 2.6 ml (4.2 mmol) of *n*-butyllithium (1.56 *M* in hexane) was added dropwise. Stirring was continued for 30 min, followed by addition of 855 mg (4.3 mmol) of *p*-(1-bromoethyl)toluene in 1.5 ml of THF. After addition was complete, the reaction mixture was warmed to room temperature and stirring was continued for 1 hr. The reaction mixture was quenched at 0° by the addition of 4 ml of 5% hydrochloric acid and the product was isolated by extraction with chloroform. After purification by passing through a column of silica gel (hexane–benzene–ethanol, 6:2:3) there was obtained 575 mg of phosphonate **4** (50% yield): ν_{max} ($CHCl_3$) 1710 cm^{-1}; nmr (CCl_4) δ 7.02 (s, 4 H), 3.67 (d, J = 11 Hz, 3 H), 3.60 (d, J = 11 Hz, 3 H), 2.92 (d, J = 22 Hz, 2 H), 2.26 (s, 3 H), 1.10 (d, 3 H); *m/e* 284.

(±)-*ar*-Turmerone.—To a suspension of 72 mg (1.7 mmol) of sodium hydride (57% dispersion; washed with hexane prior to use) in 5 ml of freshly distilled dimethoxyethane (DME) was added 436 mg (1.5 mmol) of phosphonate **4** in 0.5 ml of DME. After anion formation was complete (1.5 hr), the reaction mixture was cooled to 0° while 0.35 ml (4.8 mmol) of dry acetone was added dropwise. After addition was complete, the reaction mixture was heated to 55° and maintained at that temperature for 14 hr.

The reaction mixture was quenched by pouring it into 50 ml of a 50% aqueous sodium chloride solution. The product was ex-

(1) H. Rupe and A. Gassmann, *Helv. Chim. Acta*, **19**, 569 (1936).

(2) (a) J. Colonge and J. Chambion, *C. R. Acad. Sci.*, **222**, 557 (1946); (b) R. P. Gandhi, O. P. Vig, and S. M. Mukherji, *Tetrahedron*, **7**, 236 (1959); (c) R. J. Crawford, W. F. Erman, and C. D. Broaddus, *J. Amer. Chem. Soc.*, **94**, 4298 (1972).

(3) P. A. Grieco and C. S. Pogonowski, *J. Amer. Chem. Soc.*, **95**, 3071 (1973).

(4) B. A. Arbusov, *Pure Appl. Chem.*, **9**, 307 (1964).

(5) E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, **88**, 5654 (1966).

(6) Microanalyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Precoated plc silica gel F-254 Merck plates were used for preparative tlc. The following spectrometers were used: nmr, Varian A-60D; ir, Perkin-Elmer Model 247; mass spectrum, LKB-9.

(7) F. A. Cotton and R. A. Schunn, *J. Amer. Chem. Soc.*, **85**, 2394 (1963).

tracted with an ether–hexane mixture (3:1) and the combined extracts were dried over anhydrous magnesium sulfate. Preparative thin layer chromatography on silica gel afforded 165 mg (52%) of pure (±)-*ar*-turmerone (1): ν_{max} ($CHCl_3$) 1685 (C=O), 1620 (C=CH–), 1515 (–C_6H_4–), 819 cm^{-1} (*p*-C_6H_4–); nmr (CCl_4) δ 7.00 (s, 4 H, *p*-$CH_3C_6H_4$–), 5.90 [m, 1 H, –CH=C(CH_3)$_2$], 3.20 [m, 1 H, $C_7H_7CH(CH_3)$–], 2.50 (m, 2 H, –CH_2CO–), 2.25 (s, 3 H, *p*-$CH_3C_6H_5$–), 2.08 [s, 3 H, –COCH=C(CH_3)$_2$, methyl cis to carbonyl], 1.81 [s, 3 H, –COCH=C(CH_3)$_2$, methyl trans to carbonyl], 1.20 [d, 3 H, $C_7H_7CH(CH_3)$–]; *m/e* 216. The analytical sample was obtained as a colorless oil by preparative tlc followed by molecular distillation, bp (bath) 90° (0.07 mm).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.42; H, 9.32.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—1, 38142-58-4; 2, 4202-14-6; 4, 40601-28-3; 5, 40601-29-4.

An Improved Synthesis of 2-Methoxypropene[1]

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Received March 13, 1973

The advantages of the use of 2-methoxypropene[2] (1), 1-methoxycyclohexene (2), and 4-methoxy-5,6-dihydro-2*H*-pyran (3), over dihydropyran (4), for the protection of alcohol functions have been discussed.[3] The reaction of 1 with allylic alcohols to form allyl vinyl ethers which rearrange on heating to γ,δ-unsaturated ketones has been described.[4] Because we were interested in another use for 1, we sought to improve the tedious methods for preparation described.[5]

The improved method described herein involves adding acetone dimethyl ketal to a solution of succinic anhydride and benzoic acid[6] in pyridine and diethylene glycol dimethyl ether (diglyme) at 110–120°. The desired 1 distills as formed in excellent yield. An 8-mol run can be completed in 2–2.5 hr. When acetic anhydride[4] is used in place of succinic anhydride, methyl acetate codistills with 1 and an aqueous alkaline hydrolysis of the mixture is necessary to obtain pure 1.

The method using succinic anhydride is mainly valuable when a low-boiling vinyl ether is desired. In the case of the formation of α-methoxystyrene from acetophenone dimethyl ketal the method using succinic anhydride requires an aqueous work-up and hence has no advantage over that using acetic anhydride, but the example is given to indicate the generality of the method.

(1) This work was supported by Grant 12554 of the National Science Foundation.

(2) A. F. Kluge, K. G. Untch, and John H. Fried, *J. Amer. Chem. Soc.*, **94**, 7827 (1972).

(3) C. B. Reese, R. Saffhill, and J. E. Sulston, *J. Amer. Chem. Soc.*, **89**, 3366 (1967).

(4) G. Saucy and R. Marbet, *Helv. Chim. Acta*, **50**, 2091 (1967); R. Marbet and G. Saucy, *ibid.*, **50**, 2095 (1967).

(5) L. Claisen, *Chem. Ber.*, **31**, 1019 (1898); G. Saucy and R. Marbet, *Helv. Chim. Acta*, **50**, 1158 (1967).

(6) The reaction takes place much more slowly if benzoic acid is omitted.

Experimental Section

2-Methoxypropene (1).—To a stirred solution at 110–120° of 820 g (8.2 mol) of succinic anhydride and 24 g (0.2 mol) of benzoic acid in 640 g (8 mol) of pyridine and 600 ml of diglyme in a 3-l. three-necked round-bottomed flask fitted with a pressure-equalizing addition funnel, thermometer, and an efficient fractionating column[7] was added 832 g (8 mol) of acetone dimethyl ketal over 1.5 hr. Shortly after the ketal addition was commenced 1 distilled. After about 2 hr 547 g (95%) of 1 was obtained as a colorless liquid, bp 37°. This product, nmr (CCl_4, TMS δ 0.0) 3.80 (s, 2, $=CH_2$), 3.48 (s, 3, CH_3O–), 1.75 (s, 3, CH_3C), had a strong ir band (20% in CCl_4) at 6.08 μ (1640 cm^{-1}) for an olefin and no bands at 3.00 (3350 cm^{-1}, methanol), or near 5.8 μ (1750 cm^{-1}, acetone).

That the amount of pyridine used can be greatly decreased was shown by a similar experiment in which 208 g (2.0 mol) of acetone dimethyl ketal was added during 20 min to a solution at 110–120° of 220 g (2.2 mol) of succinic anhydride and 12 g (0.1 mol) of benzoic acid in 250 ml of diglyme and 16 g (0.2 mol) of pyridine. The yield of pure 1 obtained in 70 min was 130 g (90%).

α-Methoxystyrene (2).—To a solution at 110–120° of 33 g of succinic anhydride and 1.2 g of benzoic acid in 30 ml of pyridine and 35 ml of diglyme was added 46 g of acetophenone dimethyl ketal during 15 min. After a further 15 min the mixture was cooled and added to 200 ml of 2 *N* potassium hydroxide. The neutral product was extracted with ether and worked up in a conventional way to yield 36.0 g (97%) of 2, bp 114° (50 mm).[8]

Registry No.—1, 116-11-0; 2, 4747-13-1; acetone dimethyl ketal, 77-76-9; acetophenone dimethyl ketal, 4316-35-2.

(7) We used a 1.75 × 60 cm column packed with stainless steel heligrad packing. However, a 1.75 × 30 cm column packed with 0.25-in. glass helices worked almost as well.

(8) S. Winstein and L. L. Ingraham, *J. Amer. Chem. Soc.*, **77**, 1738 (1955), gave bp 85–89° (20 mm).

Improved Synthesis of Deuterated Olefins from the Wittig Reaction

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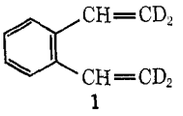
Received March 13, 1973

The utility of the Wittig reaction[1] for the synthesis of deuterated alkenes has been plagued by the occurrence of extensive deuterium scrambling and exchange with the reaction medium. Atkinson and coworkers[2] found that *n*-propyl- or *n*-butyllithium should be used as a base rather than the anion of dimethyl sulfoxide[3] in order to minimize deuterium exchange *via* enolization of the carbonyl compound. However, work-up procedures are tedious and yields are characteristically low.

In the course of some spectroscopic studies, we required a sample of *o*-divinylbenzene-d_4 (1). Survey of the literature revealed a synthesis[4] from Ph_3PCD_3Br



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(1) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954).

(2) J. G. Atkinson, M. H. Fisher, D. Horley, A. T. Morse, R. S. Stuart, and E. Synnes, *Can. J. Chem.*, **43**, 1614 (1965).

(3) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).

(4) M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, **93**, 6615 (1971).