Since complexing occurs solely at the carbonyl group of the A ring, at those concentrations given in Table I, the effect observed, $\Delta\nu$(C-B) equal to 12 Hz, must be transmitted through at least seven carbon atoms. This long-range effect is quite unexpected, since in aliphatic noncyclic bases previously studied the $\Delta\nu$-(C-B) values attenuate rapidly with distance. For example, in di-*n*-butyl ether,[20] the $\Delta\nu$(C-B) value for the methylene protons adjacent to the coordinated oxygen atom is approximately 80 Hz, whereas the terminal methyl group pmr signal is displaced only 6 Hz. Thus the 15 proton of **4** must be strongly affected by changes in the A ring.

These results demonstrate the advantages of this direct low temperature nmr method for investigating a variety of Lewis acid–base interactions involving structurally complex ligand molecules. The combination of ^{1}H and ^{19}F nmr provides a reliable method for determining the interaction site or sites in the ligand. For polyfunctional compounds the relative basicities of different sites thus can be determined. If BF_3 coordinates at each of two possible sites, they probably differ in basicity by less than 1 pK_{BH^+} unit.[8] This method could be of particular value in the steroid field, where quantitative data on basicities of functional groups are scarce.[17] Such knowledge could be used in explaining and predicting the course of acid-catalyzed reactions, although of course factors other than basicity also must be considered. For example, ketalization of **3** with methanol in the presence of *p*-toluenesulfonic acid gave largely the 3-ketal,[21] which is in accord with our finding of predominant binding of BF_3 at the 3-carbonyl. The observation of exclusive complexing at the conjugated carbonyl group of **2** and **4** also is consistent with numerous selective acid-catalyzed reactions of steroids of this type.[19] The fact that BF_3 itself frequently is used as a catalyst for steroid reactions adds to the value of the method reported here.

Acknowledgment.—We thank Dr. Anthony Fratiello for helpful discussions during the course of this work.

Registry No.—1-BF_3, 40715-58-0; 2-BF_3, 40715-59-1; **3**-2BF_3, 40715-60-4; 4-BF_3, 40758-67-6; 4-2BF_3, 40758-68-7.

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Notes

Organophosphorus Enamines. VIII. A Convenient Preparation of Diethyl β-Ketophosphonates[1]

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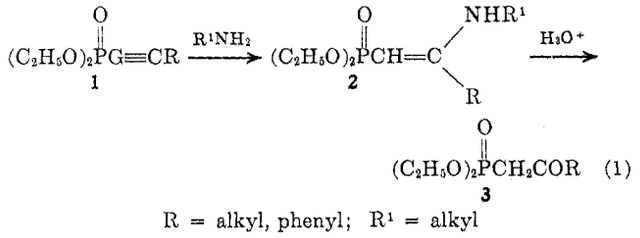
Recently we described the nucleophilic addition of aliphatic amines to the carbon–carbon triple bond in diethyl 1-alkynylphosphonates **1**,[2] giving enamine phosphonates **2** in fair to good yields.[3] Now we wish to report that an acid hydrolysis of **2** produces β-ketophosphonates **3** in excellent yields (eq 1). Compounds



(1)

R = alkyl, phenyl; R^1 = alkyl

3 prepared in this manner are listed in Table I along with their boiling points and yields.

TABLE I

Compd	R	Bp, °C (mm)	Yield,[a] %
a	*n*-C_5H_{11}	130 (0.15)	94
b	*n*-C_6H_{13}	125 (0.10)	89
c	*n*-C_7H_{15}	139 (0.1)	83
d	$(CH_3)_2CHCH_2CH_2$	137 (0.15)	91
e	*c*-C_5H_9	110 (0.10)	76
f	*c*-C_6H_{11}	151 (0.50)	81
g	C_6H_5	135 (0.10)	90
h	$C_6H_5CH_2CH_2$	162 (0.12)	91
i	$C_6H_5CH_2CH_2CH_2$	155 (0.08)	92

[a] This is the yield of the distilled material based upon the starting 1-alkynylphosphonates **1**.

The ir spectra of compounds **3a–i** display strong absorption at τ 5.85–5.90 (C=O). In the nmr spectra of **3a–i**, the *P*-methylene protons exhibit a doublet (J_{PH} = 22.5 Hz) in the region of δ 3.08–3.18. The methylenes from the *O*-ethyl groups display two quartets (J_{HH} = 7.5, J_{PH} = 9 Hz) at δ 4.12–4.20, which overlap to give a near quintet pattern. All other proton resonances were also found to be in agreement with the assigned structures. The structures were further supported by the elemental analyses of these phosphonates **3**.

The hydration of the triple bond in diethyl 1-alkynylphosphonates **1** to produce diethyl β-ketophosphonates **3** has also been reported;[4] our alternate method described here affords, under very mild conditions, a straightforward and high-yield synthesis of this very useful class of phosphonates.

(1) The work was initiated at Tulane University, New Orleans, La.
(2) M. S. Chattha and A. M. Aguiar, *J. Org. Chem.*, **36**, 2719 (1971).
(3) M. S. Chattha and A. M. Aguiar, *J. Org. Chem.*, in press.
(4) G. Sturtz and C. Charrier, *C. R. Acad. Sci.*, **261**, 1019 (1965).

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.

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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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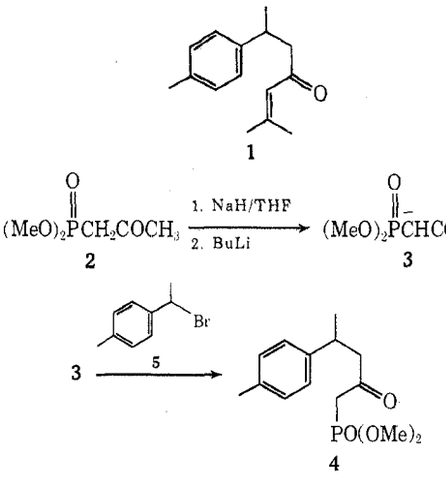
The monocyclic aromatic sesquiterpene (±)-*ar*-turmerone (**1**) is the chief component of the essential oil from the rhizomes of *Curcuma Longa* Linn.[1] Although the structure of **1** has been confirmed by a number of syntheses,[2] we would like to describe a two-step synthesis of turmerone employing 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-

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(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).