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, $C_7H_7\mathbf{CH}(CH_3)-$], 2.50 (m, 2 H, $-CH_2CO-$), 2.25 (s, 3 H, p-$\mathbf{CH_3}C_6H_5-$), 2.08 [s, 3 H, $-COCH{=}C(\mathbf{CH_3})_2$, methyl cis to carbonyl], 1.81 [s, 3 H, $-COCH{=}C(CH_3)_2$, methyl trans to carbonyl], 1.20 [d, 3 H, $C_7H_7CH(\mathbf{CH_3})-$]; *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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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.

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.

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(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).

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(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.

(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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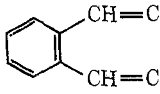
The utility of the Wittig reaction[1] for the synthesis of deuterated alkenes has been plagued by the occurrence of extensive deuterium scrambling and exchange with the reaction medium. Atkinson and coworkers[2] found that *n*-propyl- or *n*-butyllithium should be used as a base rather than the anion 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



1

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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).

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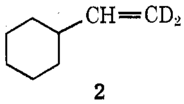
and *o*-phthalaldehyde employing *tert*-butyllithium as base. ^1H nmr analysis indicated 93% incorporation of four deuteriums, but the yield of **1** was only 1.5%. We wish to report a 20-fold increase in the yield of **1** with no apparent scrambling of deuterium *via* a simple modification of the decomposition procedure of the intermediate betaine. The method is shown to be generally applicable to other vinyl compounds, exemplified by vinylcyclohexane-d_2 (**2**).



2

Rather than employing a thermal decomposition of the betaine by refluxing for several hours,[4] we find that addition of excess D_2O gives a 30% yield of **1** and a 70% yield of **2**. ^1H and ^{13}C nmr analysis[5] indicates 97 ± 3% **1**-d_4 and 97 ± 3% **2**-d_2 deuterated *solely* at the exo methylene carbons.

Notably, if *n*-butyllithium is used as base followed by D_2O work-up, measurable exchange occurs at the exocyclic carbons in all compounds studied. Mass spectral determination indicated that d_2 material was the main impurity in the preparation of **1** and d_1 material in the case of **2**. The absence of exchange when *tert*-butyllithium is employed as base may be explained on steric grounds. Owing to the inductive effects of the methyl groups, the *tert*-butyl carbanion is expected to be a stronger base, thermodynamically, than *n*-butyllithium. The *n*-butyl carbanion, however, can approach an acidic proton with less steric restriction and thus may be the stonger base kinetically, causing exchange at the intermediate betaine stage of the reaction.

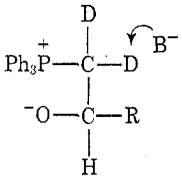
The need for an appreciable "deuterium pool" in the work-up is clear from H_2O quenching experiments in which 10–40% exchange occurs, regardless of the base employed, to give mainly **1**-d_2 and **2**-d_1, respectively. Results of several exchange experiments are presented in Table I.

TABLE I

DEUTERIUM INCORPORATIONS FROM WITTIG REACTIONS (±3%)

Salt	Base	Quenching agent	% **1**-d_4	% **2**-d_2
Ph_3PCD_3Br	*n*-BuLi	D_2O	91	84
Ph_3PCD_3Br	*t*-BuLi	D_2O	97	97
Ph_3PCD_3Br	*n*-BuLi	H_2O	81	63
Ph_3PCD_3Br	*t*-BuLi	H_2O	93	68

It is interesting that the amount of exchange decreases with increasing steric hindrance in the substrate, a finding in accord with the steric approach control argument presented above. Although the precise mechanism of isotopic exchange is difficult to elucidate, the lack of observable scrambling at the methine olefinic carbon indicates the absence of exchange in the parent aldehyde. It is proposed that scrambling of label occurs in the betaine intermediate A.



A

Experimental Section

Spectra.—^1H nmr spectra were recorded on Varian T-60 and XL-100-12 nmr spectrometers at 60 and 100 MHz, respectively. ^{13}C spectra were recorded at 25.2 MHz on the XL-100-12 under conditions of complete proton noise decoupling. Mass spectra were recorded using a Varian Anaspec EM-600.

Materials.—Methyl-d_3-triphenylphosphonium bromide was prepared from triphenylphosphine and methyl bromide-d_3 (99.5%, obtained from Stohler Isotope Chemicals, Montreal) according to the method of Trippett.[6]

A typical procedure for preparation of **2** follows. Methyl-d_3-triphenylphosphonium bromide (5.4 g, 0.015 mol) in 60 ml of dry diethyl ether were placed in a 250-ml three-necked flask under nitrogen and the suspension was stirred for 20 min. To this was added 7.1 ml of a 2.1 *M* solution of *tert*-butyllithium in pentane *via* a hypodermic syringe. The resulting orange-yellow solution was stirred for 4 hr at room temperature, then cooled to 10° *via* an ice–water bath, and 1.68 g (0.015 mol) of cyclohexanecarbonaldehyde in 20 ml of ether was added over 1 min. The resulting heavy white suspension was stirred for 10 min and then quenched by the addition of 30 ml of D_2O. The reaction mixture was extracted with three 30-ml portions of ether and dried over anhydrous magnesium sulfate. Removal of the solvent by distillation at atmospheric pressure yielded an oil containing residual triphenylphosphine oxide and vinylcyclohexane. Addition of 15 ml of petroleum ether (bp 30–60°) caused precipitation of the oxide, which was removed by filtration. Final purification of the olefin was accomplished by column chromatography (neutral alumina, activity grade I) using ether as eluent. A 71% yield of vinylcyclohexane-d_2 was obtained.

Acknowledgment.—We thank the National Research Council of Canada for financial support.

Registry No.—**2**, 40600-04-2; methyl-d_3-triphenylphosphonium bromide, 1787-44-6; cyclohexanecarbonaldehyde, 2043-61-0.

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Orientation in Base-Promoted β Eliminations from Chlorocyclodecane. The Role of Base Association

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A striking control of orientation by choice of base in eliminations from chlorocyclodecane (**1**) has been reported by Traynham, Stone, and Couvillion.[1] Reaction of **1** with *t*-BuOK in DMSO produced 97% *cis*-cyclodecene. With lithium dicyclohexylamide [$LiN(Cy)_2$] in ethyl ether–hexane, 96% *trans*-cyclodecene was obtained. Although these authors offered no explanation for this interesting dichotomy, Buehler and Pearson[2] have proposed that, in DMSO, *t*-BuOK

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[1] J. G. Traynham, D. B. Stone, and J. L. Couvillion, *J. Org. Chem.*, **32**, 510 (1967).

[2] C. A. Buehler and D. E. Pearson, "Survey of Organic Synthesis," Wiley-Interscience, New York, N. Y., 1970, p 77.