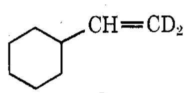
and *o*-phthalaldehyde employing *tert*-butyllithium as base. ^1H nmr analysis indicated 93% incorporation of four deuteriums, but the yield of **1** was only 1.5%. We wish to report a 20-fold increase in the yield of **1** with no apparent scrambling of deuterium *via* a simple modification of the decomposition 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.

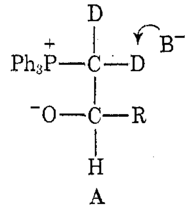
The need for an appreciable "deuterium pool" in the work-up is clear from H_2O quenching experiments in which 10–40% exchange occurs, regardless of the base employed, to give mainly **1**-d_2 and **2**-d_1, respectively. Results of several exchange experiments are presented in Table I.

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.



$$\begin{array}{c} \mathrm{D} \\ | \\ \mathrm{Ph_3\overset{+}{P}{-}C{-}D} \quad \mathrm{B^-} \\ | \\ \mathrm{^-O{-}C{-}R} \\ | \\ \mathrm{H} \end{array}$$

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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[5] J. B. Stothers, C. T. Tan, A. Nickon, F. Huang, R. Scridhar, and R. Weglein, *J. Amer. Chem. Soc.*, **94**, 8581 (1972).

[6] S. Trippett, "Advances in Organic Chemistry," Vol. 1, Interscience, New York, N. Y., 1960, pp 83–102.

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.

TABLE I

OLEFINIC PRODUCTS FROM REACTION OF CHLOROCYCLODECANE WITH VARIOUS BASE–SOLVENT SYSTEMS

Expt	Base–solvent	Conditions	% of total cyclodecenes *trans*-Cyclodecene	 *cis*-Cyclodecene
1[a]	*t*-BuOK–DMSO	5 min, room temp	18 ± 1[b]	82 ± 1
2[a]	*t*-BuOK–DMSO	15 min, room temp	6 ± 1	94 ± 1
3[a]	*t*-BuOK–DMSO	2 hr, room temp	4 ± 1	96 ± 1
4[c]	LiN(Cy)$_2$–ether–hexane	24 hr, reflux	87 ± 2	13 ± 2
5[d]	LiN(Cy)$_2$–ether–hexane[e]	3 hr, reflux	69 ± 1	31 ± 1
6[d]	LiN(Cy)$_2$–ether–hexane[e]	24 hr, reflux	68 ± 3	32 ± 3
7[f]	*t*-BuOK–*t*-BuOH	24 hr, 50°	56 ± 2	44 ± 2
8[f]	*t*-BuOK–*t*-BuOH[g]	2 hr, 50°	62 ± 1	38 ± 1

[a] [1] = 0.6 *M*, [*t*-BuOK] = 0.9 *M*. [b] Standard deviation from repetitive analysis of extracted product mixture. [c] [1] = 0.3 *M*, [LiN(C$_6$H$_{11}$)$_2$] = saturated solution. [d] [1] = 0.3 *M*, [LiN(C$_6$H$_{11}$)$_2$] = 0.3 *M*. [e] Tetramethyl-12-crown-4 (0.3 *M*) present. [f] [1] = 0.6 *M*, [*t*-BuOK] = 0.6 *M*. [g] Dicyclohexyl-18-crown-6 (0.6 *M*) present.

is well dissociated, which favors anti elimination and the formation of *cis*-cyclodecene. However, in ether–hexane, association of the cation and anion of LiN(Cy)$_2$ promotes syn elimination and the production of *trans*-cyclodecene.[3,5] Because of our interest in the effect of base association upon orientation and stereochemistry in base-promoted β-elimination reactions,[7-9] an examination of this hypothesis was undertaken.

The relative proportions of isomeric cyclodecenes which are formed in reactions of **1** with three base–solvent systems are reported in Table I. For expt 3 and 4, procedures of Traynham, Stone, and Couvillion[1] were employed on a reduced scale. Under these conditions, reactions of **1** with *t*-BuOK–DMSO and LiN(Cy)$_2$–ether–hexane produce predominantly *cis*-cyclodecene and *trans*-cyclodecene, respectively.

However, the relative amounts of *cis*- and *trans*-cyclodecene which result from reaction of **1** with *t*-BuOK–DMSO vary with reaction time (compare expt 1–3). This suggests isomerization of initially formed *trans*-cyclodecene to the thermodynamically more stable cis isomer[10] by *t*-BuOK–DMSO.[11] Exposure of a cyclodecene mixture rich in the trans isomer (68% *trans*- and 32% *cis*-cyclodecene) to the reaction conditions of expt 3 resulted in isomerization to a mixture which contained 96% *cis*-cyclodecene.[12] Therefore, the high proportions of *cis*-cyclodecene which have been observed in reactions of **1** with *t*-BuOK–DMSO result from product isomerization, not from a special effect of a dissociated base.

A relatively minor influence of base association upon orientation in eliminations from **1** was demonstrated by use of crown ethers (macrocyclic polyethers).[13] Crown ethers strongly complex alkali metal cations[13] and markedly reduce the extent of base association in solvents of low polarity.[7,8,14] Reactions of **1** with LiN(Cy)$_2$–ether–hexane and tetramethyl-12-crown-4[15,16] (expt 5 and 6) and *t*-BuOK–*t*-BuOH and dicyclohexyl-18-crown-6[13] (expt 8) produced a somewhat greater proportion of *cis*-cyclodecene than in the absence of the crown ethers (expt 4 and 7, respectively). These increases probably result from a change in elimination stereochemistry for *cis*-cyclodecene formation from mostly syn with the associated bases to predominantly anti in the presence of the crown ethers.[14]

Experimental Section

Chlorocyclodecane[1,17] and tetramethyl-12-crown-4[15] were prepared by literature methods. Commercial *t*-BuOK (MSA, sublimed), DMSO (Baker, reagent), anhydrous ethyl ether (Mallenkrodt, reagent), hexane (Baker, reagent), and methyllithium in ether (Foote) were used directly. Dicyclohexylamine (Eastman) was purified by distillation. Solutions of *t*-BuOK–*t*-BuOH were prepared as before.[18]

Procedure.—Reactant concentrations, temperatures, and times are given in Table I. Reactions of 1 with *t*-BuOK–DMSO and *t*-BuOK–*t*-BuOH were conducted by adding 1 to 5 ml of the appropriate base–solvent solution. After the desired reaction period, the reaction mixture was poured into 25 ml of water and extracted with pentane (2 × 10 ml) and the volume of the pentane solution was reduced to 2 ml. The resulting liquid was analyzed by gas–liquid chromatography on a Varian Aerograph Model 1700 flame ionization gas chromatograph using 30 ft × 0.125 in. columns of 20% UCON 50HB100 on Chromosorb P operated at 150° Reactions of 1 with LiN(Cy)$_2$ in ether–hexane were performed by adding 0.50 g (3 mmol) of 1 in 5 ml of hexane to a mixture formed by addition of 1.76 ml (3 mmol) of methyllithium in ether to 0.50 g (3 mmol) of dicyclohexylamine in 5 ml of ether. Work-up and analysis were as given above.

Isomerization Studies.—A cyclodecene mixture (68 ± 3% trans and 32 ± 3% cis) was added to a solution of 2.5 ml of 0.9 *M* *t*-BuOK–DMSO. After 2 hr at room temperature, work-up, and analysis in the usual fashion, the cyclodecene mixture was found to be predominately *cis*-cyclodecene (4 ± 1% trans and 96 ± 1% cis).

Registry No.—Chlorocyclodecane, 7541-62-0; *trans*-cyclodecene, 2198-20-1; *cis*-cyclodecene, 935-31-9.

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(3) In eliminations from cyclodecyl bromide induced by *t*-BuOK–*t*-BuOH and *t*-BuOK–benzene, *cis*-cyclodecene is formed by anti elimination and *trans*-cyclodecene by syn elimination. For reactions with *t*-BuOK–DMF and EtOK–EtOH, both cyclodecenes arise by anti elimination.[4]

(4) J. Závada, J. Krupička, and J. Sicher, *Collect. Czech. Chem. Commun.*, **33**, 1393 (1967).

(5) For discussions of the favoring of syn elimination relative to anti elimination by base association, see ref 4, 6, and 7.

(6) J. Závada and J. Svoboda, *Tetrahedron Lett.*, 23 (1972).

(7) R. A. Bartsch and K. E. Wiegers, *Tetrahedron Lett.*, 3819 (1972).

(8) R. A. Bartsch, G. M. Pruss, R. L. Buswell, and B. A. Bushaw, *Tetrahedron Lett.*, 2621 (1972).

(9) R. A. Bartsch, *J. Org. Chem.*, **38**, 846 (1973).

(10) N. L. Allinger, *J. Amer. Chem. Soc.*, **79**, 3443 (1957).

(11) The propensity of *t*-BuOK–DMSO for olefin isomerization is well known. See A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, **84**, 3164 (1962), and papers cited therein.

(12) Equilibration of cyclodecenes with lithium 2-aminoethylamide in ethylenediamine yields 96% *cis*- and 4% *trans*-cyclodecene.[4]

(13) C. J. Pederson, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 391 (1970).

(14) M. Svoboda, J. Hapala, and J. Závada, *Tetrahedron Lett.*, 265 (1972).

(15) J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959).

(16) Addition of tetramethyl-12-crown-4 caused the heterogeneous mixture of LiN(Cy)$_2$ ether–hexane to become homogeneous.

(17) We thank Cities Service Co., Cranbury, N. J., for a generous sample of cyclodecane.

(18) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 1376 (1969).