Table I. α Alkylation and α Arylation of Chloroacetonitrile with Organoboranes under the Influence of Potassium 2,6-Di-*t*-butylphenoxide[a]

Organoborane R_3B or B-R-9-BBN	Product	Yield,[b] %
Triethyl	Butyronitrile	95[c]
Tri-*n*-butyl	Hexanonitrile	89[c]
B-*n*-Butyl	Hexanonitrile	76
B-2-Butyl	3-Methylpentanonitrile	65
B-Isobutyl	4-Methylpentanonitrile	57
Tricyclopentyl	Cyclopentylacetonitrile	67[c]
B-Cyclopentyl	Cyclopentylacetonitrile	72
B-Cyclohexyl	Cyclohexylacetonitrile	77
B-*exo*-Norbornyl	2-Norbornylacetonitrile[d]	65
B-Phenyl	Phenylacetonitrile	75

[a] All reactions were carried out in tetrahydrofuran at 0° using 10 mmoles each of the organoborane, the base, and the chloroacetonitrile. [b] Glpc analysis. [c] Based on the availability of only one alkyl group per trialkylborane molecule. [d] The stereochemistry was not established, but this is probably the *exo* isomer from the apparent reaction mechanism.

tion of the base follow the procedure previously described.[5] To this solution at 0° was added 100 mmoles of tricyclopentylborane in THF, prepared from cyclopentene and THF–borane, followed by the dropwise addition of 7.5 g of chloroacetonitrile (100 mmoles) in 50 ml of THF. The reaction mixture was stirred for 1 hr. *n*-Octane was added as an internal standard; glpc analysis showed the presence of 67% cyclopentylacetonitrile. The reaction mixture was diluted with 200 ml of pentane, washed with three portions of 1 *N* sodium hydroxide, washed with water, and dried over anhydrous magnesium sulfate. Distillation gave 5.4 g (50% yield) of cyclopentylacetonitrile, bp 76–78° (15 mm), n^{20}D 1.4495 (lit.[12] n^{20}D 1.4474).

Nitriles such as *n*-butyronitrile and phenylacetonitrile proved to be quite stable to the base over 24 hr at room temperature. Consequently, we also explored the applicability of three of the modified procedures[5] in the reaction of triethylborane with chloroacetonitrile: procedure A, 95%; procedure B, 96%; procedure C, 95%. It follows that here also the precise procedure to be selected appears to be primarily a matter to be decided on the basis of convenience—all give excellent yields.

(12) R. C. Elderfield and E. T. Losin, *J. Org. Chem.*, **26**, 1703 (1961).
(13) Visiting scholar on funds provided by the Mitsui Petrochemical Industries, Ltd., Tokyo, Japan.

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Reaction of Organoboranes with Ethyl Bromoacetate and Ethyl Dibromoacetate under the Influence of Potassium 2,6-Di-*t*-butylphenoxide, an Unusual Base with Large Steric Requirements

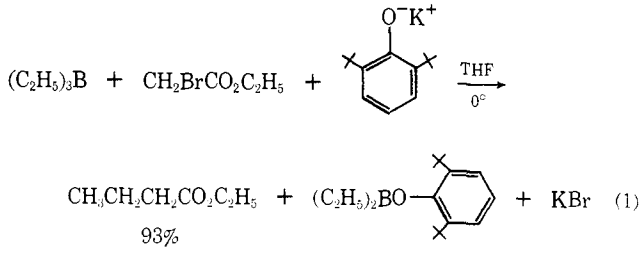
Sir:

In the preceding communications we described the fast reactions of organoboranes with bromoacetone[1] and chloroacetonitrile[2] under the influence of potassium 2,6-di-*t*-butylphenoxide and reported some of the unusual properties of this base. Thus representative ketones, such as acetone, cyclohexanone, and acetophenone, appear to be quite stable to the base at 25° over considerable periods of time, whereas the same ketones at 0° react in a matter of seconds with potassium *t*-butoxide.[1] Similarly, nitriles, such as butyronitrile and phenylacetonitrile, are stable to the phenoxide base.[2] This property is quite valuable in permitting the synthesis of ketones and nitriles by the organoborane route in the presence of excess base without loss of product.[1,2] Excess potassium *t*-butoxide must be carefully avoided in the related syntheses utilizing this base.[3,4]

Presumably, the marked difference in the behavior of the two bases is a consequence of the great difference in their base strengths. An indication of this great difference is provided by a comparison of the pK_a for *t*-butyl alcohol, 19,[5] with that for 2,6-di-*t*-butylphenol, 11.7.[6] (At the same time it should be kept in mind that the base strengths in aprotic solvents, such as tetrahydrofuran or dimethyl sulfoxide, do not necessarily correlate with the pK_a values measured in hydroxylic media.)

Preliminary experiments revealed that esters, such as ethyl butyrate and ethyl phenylacetate, are also quite stable to the base in THF at 25°, whereas these same esters rapidly disappear from a THF solution of potassium *t*-butoxide at 0°. Consequently, it appeared that the new base might also have advantages in making possible the synthesis of esters from organoboranes without the usual requirement of protecting the product from excess base.[3]

Indeed, we observed that nearly quantitative yields of ethyl butyrate were realized from the reaction of triethylborane and ethyl bromoacetate under the influence of potassium 2,6-di-*t*-butylphenoxide in THF solution



at 0° (eq 1). We examined the effect of modification of the experimental procedure. The base was prepared from potassium metal and the phenol (20% excess) in THF and the ethyl bromoacetate was added to an equimolar mixture of the base and triethylborane; yield 93%. The base was prepared by adding potassium *t*-butoxide in THF to the phenol and triethylborane in THF and the reaction achieved by adding ethyl bromoacetate to the mixture; yield 96%. In the third procedure the base was generated by adding an equal volume of a solution of potassium *t*-butoxide in *t*-butyl alcohol to the phenol and triethylborane in THF; yield 95%. Evidently all of these procedures are quite satisfactory.

(1) H. C. Brown, H. Nambu, and M. M. Rogić, *J. Am. Chem. Soc.*, **91**, 6852 (1969).
(2) H. C. Brown, H. Nambu, and M. M. Rogić, *ibid.*, **91**, 685 (1969).
(3) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968).
(4) H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **90**, 6218 (1968).
(5) For a summation of data on acidities of active hydrogen in representative derivatives, see H. O. House, "Modern Synthetic Methods," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 7.
(6) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963).

The reaction works equally well for the monoalkylation of ethyl dibromoacetate to produce ethyl α-bromobutyrate (eq 2). By utilizing 2 moles of base and 2

$$(C_2H_5)_3B + CHBr_2CO_2C_2H_5 \xrightarrow[0°]{THF,\ B} CH_3CH_2\underset{\underset{Br}{|}}{C}HCO_2C_2H_5 \quad (2)$$

83%

moles of triethylborane, dialkylation was achieved (eq 3).

$$2(C_2H_5)_3B + CHBr_2CO_2C_2H_5 \xrightarrow[25°]{THF,\ 2B} (C_2H_5)_2CHCO_2C_2H_5 \quad (3)$$

66%

In these reactions we evidently utilize satisfactorily only one of the three alkyl groups on boron. This is a major disadvantage when one wishes to homologate a reaction intermediate in high yield. Fortunately, use of the B-alkyl-9-borabicyclo[3.3.1]nonanes (B-R-9-BBN) circumvents this difficulty in the procedures previously reported.[7,8] However, when we attempted to use B-ethyl-9-BBN to alkylate ethyl bromoacetate with potassium 2,6-di-*t*-butylphenoxide in THF, the yield dropped to 0!

Since the bromo ester had disappeared from the reaction mixture, the reaction must be taking another course. We considered the possibility that the reaction involved a migration in the intermediate of the cyclooctyl–boron bond, rather than the desired ethyl–boron bond, as observed in the reaction of B-*n*-butyl-9-BBN with ethyl diazoacetate.[8,9] However, examination of the reaction mixture, following oxidation with alkaline hydrogen peroxide, revealed the absence of ethyl *cis*-5-hydroxycyclooctylacetate, the product formed in such a migration of the cyclooctyl–boron bond.[8]

We then concluded that the difficulty must lie in the slow protonolysis of the rearranged boron intermediate, so that it is capable of reacting competitively with freshly formed α-bromo carbanions. We are exploring this question. Fortunately, the presence in the reaction mixture of *t*-butyl alcohol overcame the difficulty, whatever it may be.

Our final procedure involves making a 1 *M* solution of the organoborane in THF by the usual methods, adding an equimolar quantity of 2,6-di-*t*-butylphenol, followed by addition of a 1 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol. The reaction mixture is thus roughly 50:50 in THF and *t*-butyl alcohol. To this reaction mixture at 25° is added the bromo ester. With this procedure, both the trialkylboranes and the 9-alkyl-9-BBN reagents react satisfactorily.

The experimental results are summarized in Table I.

Perhaps the most unexpected feature about this development is the great speed and ease with which potassium 2,6-di-*t*-butylphenoxide is capable of bringing about these reactions. Certainly, the low pK_a value of the phenol, 11.7,[6] would not lead one to anticipate that it would be so effective in removing a proton from the α position of the α-halo ketones, nitriles, and esters (pK_a values[5] of the parent structures 20, 25, 24, respectively). Potassium *t*-butoxide is a far stronger base in tetrahydrofuran and dimethyl sulfoxide than in *t*-butyl alcohol. Presumably, this is due to the fact that the activity of the anion is not reduced by strong solvation. Perhaps the bulky substituents in 2,6-di-*t*-butylphenol serve a similar function in separating both the cation and solvent from the charged oxygen atom, so that the base is more effective in removing an active methylene hydrogen than one would predict from its pK_a value. Combined with the large steric requirements that prevent it from coordinating with trialkylboranes, it is evident that it must be considered an ideal base for the reactions under consideration.

We have not yet explored its utility as a basic catalyst for other types of reactions, such as Darzen's condensation and the Michael addition. However, it is evident that its unusual characteristics also offer promise in such applications.

Table I. α Alkylation of Ethyl Bromoacetate and Dibromoacetate with Organoboranes under the Influence of Potassium 2,6-Di-*t*-butylphenoxide[a]

Organoborane, R_3B or B-R-9-BBN	Bromo ester	Product	Yield,[b] %
Triethyl	Br	Ethyl butyrate	95
B-Ethyl	Br	Ethyl butyrate	70
B-Isobutyl	Br	Ethyl isovalerate	56
Tricyclopentyl	Br	Ethyl cyclopentylacetate	75
B-Cyclopentyl	Br	Ethyl cyclopentylacetate	57
Triethyl	Br_2	Ethyl α-bromobutyrate	96
B-Ethyl	Br_2	Ethyl α-bromobutyrate	83
B-Isobutyl	Br_2	Ethyl α-bromoisovalerate	81
Tricyclopentyl	Br_2	Ethyl α-bromocyclopentylacetate	76
B-Cyclopentyl	Br_2	Ethyl α-bromocyclopentylacetate	78

[a] Reaction was carried out in a 50:50 THF–*t*-butyl alcohol medium at 25°. [b] Yields by glpc analysis.

(10) Visiting scholar on funds provided by the Mitsui Petrochemical Industries, Ltd., Tokyo, Japan.

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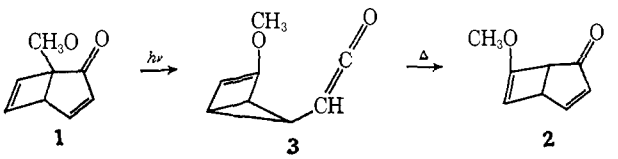
Photochemistry of Bicyclic Dienones. A Homoelectrocyclic Reaction[1]

Sir:

The photoisomerization of 1-methoxybicyclo[3.2.0]-hepta-3,6-dienone (**1**) to 7-methoxybicyclo[3.2.0]hepta-3,6-dienone (**2**) has been shown to proceed *via* a ketene



1 **3** **2**

intermediate (**3**). Attempts to trap the intermediate have been unsuccessful because of the facile thermal isomerization of the ketene.[2] In a search for analogous reactions in which the intermediate ketenes might be

(7) H. C. Brown and M. M. Rogić, *J. Am. Chem. Soc.*, **91**, 2146 (1969).
(8) H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969).
(9) J. Hooz and S. Linke, *ibid.*, **90**, 5936, 6891 (1968).

(1) Photochemical Transformations. XXXV.
(2) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968).