to be adopted should depend primarily on convenience in a particular situation.

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

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Reaction of Organoboranes with Chloroacetonitrile under the Influence of Potassium 2,6-Di-t-butylphenoxide. A Convenient Procedure for the Conversion of Olefins into Nitriles via Hydroboration

Sir:

Trialkylboranes react, under the influence of potassium t-butoxide (in t-butyl alcohol or tetrahydrofuran), with ethyl haloacetate, ethyl dihaloacetate, and various \( \alpha \)-halo ketones to give the \( \alpha \)-alkylacetate (eq 1), the \( \alpha \)-alkyl-\( \alpha \)-haloacetate (eq 2), the \( \alpha,\alpha \)-dialkylacetate (eq 3), and the corresponding \( \alpha \)-alkyl ketones (eq 4).

\[
R_3B + CH(X)CO_2C_6H_5 \rightarrow RCH(X)CO_2C_6H_5 \quad (1)
\]

\[
R_3B + CH(X)CO_2C_6H_5 \rightarrow CH(X)CO_2R_3 \quad (2)
\]

\[
2R_3B + CH(X)CO_2C_6H_5 \rightarrow R_3CHCO_2CH_3 \quad (3)
\]

\[
R_3B + CHCOR' \rightarrow RCHCOR' \quad (4)
\]

All attempts to extend the reaction to the synthesis of nitriles by a related alkylation of chloroacetonitrile under the influence of potassium t-butoxide had been unsuccessful. Our success in achieving the alkylation of two-carbon moiety to the molecule and to the various derivatives to which nitriles are readily converted (amines, amides, carboxylic acids) (eq 5, 6).

\[
(C_3H_5)_3B + CHCN \rightarrow \text{aryl} + \text{KCl} \quad (5)
\]

\[
\text{C}_3\text{H}_5\text{CN} + (C_3H_5)B-O-C_6H_5 \rightarrow \text{KCl} \quad 77\%
\]

In the corresponding reaction with bromoacetone, it was noted that protonolysis of the reaction intermediate by the 2,6-di-t-butylphenol produced in the reaction was relatively difficult. Consequently, ethanol was added to liberate the ketone. However, in the present case the reaction intermediate evidently undergoes protonolysis much more readily, so that examination of the reaction mixture by glpc revealed the presence of the product in high yield without adding ethanol or other protonolysing agent.

Recently Hooz and Linke have reported that diazoacetonitrile, diazoacetonitrile, and ethyl diazoacetate react with trialkylboranes to yield the corresponding ketones, nitriles, and esters. These reactions provide an important new route to these derivatives.

In all of these reactions only one of the three groups of a trialkylborane is utilized. This limitation could constitute a major difficulty in cases where it is desired to apply these homologation reactions to valuable intermediates. Fortunately, the use of the B-aryl-9-borabicyclo[3.3.1]nonane derivatives (B-R-9-BBN) circumvented this difficulty for the base-induced synthesis of esters and ketones. The same expedient served for the present nitrile synthesis (eq 7).

\[
\text{CHCN} + (B-O-C_6H_5) \rightarrow \text{KCl} \quad (6)
\]

The new B-aryl-9-BBN reagents also were satisfactory to achieve \( \alpha \) arylation of chloroacetonitrile (eq 8). The experimental results are summarized in Table I.

\[
\text{C}_3\text{H}_5\text{CN} + \text{KCl} \rightarrow \text{CH}_3\text{CN} \quad 75\%
\]

The procedure is indicated by the preparation of cyclopentylacetonitrile. The apparatus and the prepara-

(6) J. Hooz and S. Linke, ibid., 90, 5936 (1968).
(7) J. Hooz and S. Linke, ibid., 90, 6891 (1968).
(10) We did not attempt to see whether the B-R-9-BBN derivatives would solve this difficulty with diazoacetonitrile. Previously, we had observed that these derivatives did not overcome the problem with ethyl diazoacetate.
Table I. Alkylation and Aroylation of Chloroacetonitrile with Organoboranes under the Influence of Potassium 2,6-Di-t-butylphenoxide

<table>
<thead>
<tr>
<th>Organoborane</th>
<th>Product</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethyl</td>
<td>Butyronitrile</td>
<td>95</td>
</tr>
<tr>
<td>Tri-n-butyl</td>
<td>Hexanenitrile</td>
<td>89</td>
</tr>
<tr>
<td>B-n-Butyl</td>
<td>Hexanenitrile</td>
<td>76</td>
</tr>
<tr>
<td>B-2-Butyl</td>
<td>3-Methylpentalonitrile</td>
<td>65</td>
</tr>
<tr>
<td>B-Isobutyl</td>
<td>4-Methylpentalonitrile</td>
<td>57</td>
</tr>
<tr>
<td>Tricyclopentyl</td>
<td>Cyclopentylacetonitrile</td>
<td>67</td>
</tr>
<tr>
<td>B-Cyclopentyl</td>
<td>Cyclopentylacetonitrile</td>
<td>72</td>
</tr>
<tr>
<td>B-Cyclohexyl</td>
<td>Cyclohexylacetonitrile</td>
<td>77</td>
</tr>
<tr>
<td>B-norbornyl</td>
<td>2-Norbornylacetonitrile</td>
<td>65</td>
</tr>
<tr>
<td>B-Phenyl</td>
<td>Phenylacetonitrile</td>
<td>75</td>
</tr>
</tbody>
</table>

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

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. Similarly, nitriles, such as butyronitrile and phenylacetonitrile, are stable to the phenoxide base. 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. Excess potassium t-butoxide must be carefully avoided in the related syntheses utilizing this base.

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 values of dimethylformamide, the solvents, such as acetone, cyclohexanone, and acetophenone, 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.

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; yield 96%. Evidently all of these procedures are quite satisfactory.

At this stage 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.

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