CONCLUSIONS

The acylation of alkynes by α-bromobutyroyl tetrafluoroborate under "nonnucleophile" conditions takes place as a reaction involving the conjugated addition of the acylium cation and the bromide anion from the acyl residue over the triple bond by means of a 1, 4 shift.

LITERATURE CITED


INTERMEDIATES IN ELECTROPHILIC VINYL SUBSTITUTION IN 1,1-DIARYLETHYLENES AND REDUCTION OF β-SUBSTITUTED 1,1-DIARYLETHYL CATIONS BY TRIETHYLSILANE

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The reaction of 1,1-diarylethenes with mercuric trifluoroacetate or mercuric nitrate in CH₃CN, ether, benzene, or another aprotic solvent results in the substitution of the vinyl hydrogenby mercury [1]. This process is analogous to the previously known vinyl bromination reaction in [2] and several other electrophilic vinyl substitution reactions in 1,1-diarylethenes [3].

The intermediates of mercuration and halogenation reactions have been studied with the aid of UV, ¹H NMR, and ¹³C NMR spectroscopy [4]. The data obtained are evidence in favor of the asymmetric structure of the intermediate with predominant localization of the positive charge on one carbon atom, i.e., the open structure of β-carbonium ion Ar₂C⁺–CH₂E, where E = HgOCOCF₃, Cl, Br.

The ability of carbonium ions to mediate intermolecular hydride transfer is well known. The purpose of the present work was to study hydride transfer from triethylsilane to 2-halomercuri-1,1-dialkylethyl cations, which are generated from substituted olefins or alcohols and CF₃COOH according to the scheme

\[
\begin{align*}
R₂C=CH₂ & \xrightarrow{H^+} R₂C⁺CH₂E \\
\text{OH} & \xrightarrow{H₂O} R₂C⁺CH₂E \\
R₂C=CH₂ & \xrightarrow{H^+} R₂C⁺CH₂E
\end{align*}
\]

Reduction by trialkysilanes in CF₃COOH, which is known as an ionic hydrogenation reaction [5], has not previously been applied to olefins and alcohols containing mercury or halogens.

The reactivity of β-substituted 1,1-dialkylethyl cations with respect to the hydride ion should be dependent on the distribution of the positive charges in the system, which is determined by the nature of the heteroatom. The presence of a β halogen atom creates the possibility for an intramolecular nucleophilic interaction with the carbonium center. The presence of a highly polar Hg⁶⁺–X⁻ bond introduces a second electrophilic center into the cation. Taking advantage of Pearson’s principle of hard and soft acids and bases [6, 7], we were
TABLE 1. Chemical Shifts and Spin—Spin Coupling Constants Calculated from Data from the PMR Spectra of 1,1-Diaryl-2-haloethanes (A2B systems [8])

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>δ, ppm CH</th>
<th>δ, ppm CH2</th>
<th>JAB, Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph2CHCH2Br</td>
<td>CCl4</td>
<td>4.35</td>
<td>3.83</td>
<td>8.0</td>
</tr>
<tr>
<td>Ph2CHCH2Cl</td>
<td>CCl4</td>
<td>4.25</td>
<td>3.92</td>
<td>7.8</td>
</tr>
<tr>
<td>(CH3OC12H5)2CH—CH2Br</td>
<td>CCl4</td>
<td>4.20</td>
<td>3.73</td>
<td>7.6</td>
</tr>
</tbody>
</table>

able to a priori assume the hydride, being a soft base, should preferentially attack the β-mercured cation at the softer mercury atom R—Hg. In the case of the 2-halogen-substituted ion, only the C atom bearing the positive charge is an active center.

The experiment showed that 1,1-diaryl-1-hydroxy-2-haloethanes and 1,1-diaryl-2-haloethylenes containing chlorine and bromine are converted rapidly and with a high yield into 1,1-diaryl-2-haloethanes under the action of CF3COOH and Et3SiH according to the scheme

\[
\text{H}^+ + \text{Et}_3\text{SiH} \xrightarrow{\text{Ar}_2\text{C} = \text{CHHal}} \text{Ar}_2\text{C}^+\text{CH}_2\text{Hal} \xrightarrow{\text{Et}_3\text{SiH}} \text{Ar}_2\text{C} = \text{CH}_2\text{Hal} \xrightarrow{\text{OH}} \text{Hal = Cl, Br}
\]

In the case of the formation of a stable 1,1-di(p-methoxyphenyl)-2-bromoethyl cation from 1,1-di(p-methoxyphenyl)-2-bromoethylene, the reduction proceeds so vigorously that the reaction can be carried out as a titration.

The 1,1-diaryl-2-haloethanes isolated in the experiments were characterized by elemental analysis, PMR spectra, which contained characteristic multiplets of the A2B systems of the CH—CH2 groups (Table 1), data from TLC on Silufol, and chemical conversions. 1,1-Diaryl-2-haloethanes differ with respect to their stability. The previously unknown 1,1-di(p-methoxyphenyl)-2-bromoethane is the least stable. For example, during the chromatography on Al2O3 it completely decomposed to form 1,1-di(p-methoxyphenyl)ethylene. From the samples of 1,1-diphenyl-2-bromoethane and 1,1-di(p-methoxyphenyl)-2-bromoethylene, we obtained the corresponding 2-bromomercuriethanes, which were the standards for the study of the reduction of the β-mercured cations:

\[
\text{Ar}_2\text{C} = \text{CHHal} \xrightarrow{\text{Et}_3\text{SiH}} \text{Ar}_2\text{C}^+\text{CH}_2\text{Hal} \xrightarrow{\text{Et}_3\text{SiH}} \text{Ar}_2\text{C} = \text{CH}_2\text{Hal} \xrightarrow{\text{OH}} \text{Hal = Cl, Br}
\]

The reaction was complicated by the formation of 1,1,4,4-tetraarylbutanes, which is especially significant in the case of 1,1-di(p-methoxyphenyl)-2-bromoethane. In this case, the application of column chromatography was required for the isolation of the organomercury compound.

In the preliminary experiments it was found that mercury trifluoroacetates with the general formula RHgOCOCF3, where R =OCOCF3, Ar2C=CH, or Ar2CH—CH2, react with triethylsilane in ether CH2Cl2, CHCl3, and CH3CN with the formation of metallic mercury. The only reduction products of the 2,2-diarylvinylmercury compounds were the corresponding olefins. In the case of the compounds with the formula Ar2CHCH2-HgOCOCF3, the reaction was more complicated. The reaction mixture contained the 1,1-diarylethane and 1,1-diarylethylene. Such a result may be due to the radical mechanism of the reduction of the compounds under investigation. Stepwise demercuration with the intermediate formation of an unstable mercury hydride is more likely.

\[
\text{RHgOCOCF}_3 \xrightarrow{\text{Et}_3\text{SiH}} \text{RHgH}
\]

The subsequent conversions of this intermediate to form the product involve the homolytic splitting of the C—Hg bond. It should be noted that the formation of RHgH has been postulated in most communications devoted to the reduction of organomercury compounds by hydrides [9, 10].

The foregoing reactions simulate some of the processes which take place in 2,2-diarylvinylmercury salts under the conditions of ionic hydrogenation.