Synthesis
of 1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dienylmethyl Haloacetates


Institute of Chemical Problems, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan
Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan

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Abstract—Hexachlorobicyclo[2.2.1]hepta-2,5-dienylmethyl haloacetates were prepared by [4+2]-cycloaddition of hexachlorocyclopentadiene to the corresponding propargyl haloacetates.

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Compounds of the bicyclo[2.2.1]heptene series exhibit diverse useful properties. Rigid framework structures of these compounds with fixed substituents are promising models for studying structure–property relationships [1].

Polyhalogenated bicyclic esters with other functional groups are widely used for imparting fireproof properties to polymeric materials, and also as modifiers, epoxy resin hardeners, and biologically active substances [2, 3]. Halogen-containing functionally substituted norbornenes are used as starting compounds for preparing important commercial chemicals [4–7]. Studies of reactions involving hexachlorocyclopentadiene (HCCPD) and its derivatives, along with practical significance, are of scientific interest for elucidating the mechanism of Diels–Alder reactions [8].

Proceeding with studies in the field of the synthesis of polyhalogenated bicyclic esters [9–14], we prepared and examined polyhalonorbornadienylmethyl haloacetates. First, by the esterification procedure, we prepared propargyl haloacetates IX–XV by the following scheme:

\[
\text{POCl}_3 + \text{II} + \text{III} \rightarrow \text{IX} \rightarrow \text{X} \rightarrow \text{XI} \rightarrow \text{XII} \rightarrow \text{XIII} \rightarrow \text{XIV} \rightarrow \text{XV}
\]

R = CH₂Cl (II, IX), CHCl₂ (III, X), CCl₃ (IV, IX), CH₂Br (V, XII), CHBr₂ (VI, XIII), CBr₃ (VII, XIV), CF₃ (VIII, XV).

Table 1. The physicochemical properties of the esters prepared

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_b, \degree C/P, \text{mm Hg} )</th>
<th>( n^2_5 )</th>
<th>( d^2_40 )</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propargyl monochloroacetate IX</td>
<td>70–71/10</td>
<td>1.4610</td>
<td>1.2230</td>
<td>65</td>
</tr>
<tr>
<td>Propargyl dichloroacetate X</td>
<td>75/8</td>
<td>1.4730</td>
<td>1.3615</td>
<td>55</td>
</tr>
<tr>
<td>Propargyl trichloroacetate XI</td>
<td>75–76/9</td>
<td>1.4771</td>
<td>1.4972</td>
<td>50</td>
</tr>
<tr>
<td>Propargyl monobromoacetate XII</td>
<td>79–81/10</td>
<td>1.4875</td>
<td>1.5675</td>
<td>60</td>
</tr>
<tr>
<td>Propargyl dibromoacetate XIII</td>
<td>49–51/1</td>
<td>1.4566</td>
<td>1.7270</td>
<td>60</td>
</tr>
<tr>
<td>Propargyl tribromoacetate XIV</td>
<td>84–85/1</td>
<td>1.5456</td>
<td>2.2865</td>
<td>54</td>
</tr>
<tr>
<td>Propargyl trifluoroacetate XV</td>
<td>75/3</td>
<td>1.3480</td>
<td>1.2373</td>
<td>48</td>
</tr>
</tbody>
</table>
The physicochemical properties of the esters prepared are given in Table 1.

The target products XVII–XXIII were prepared by the Diels–Alder reaction of HCCPD XVI with propargyl haloacetates IX–XV. The reaction follows the scheme

![Reaction Scheme]

The reaction was performed in the temperature range 100–180°C for 2–14 h at the diene : dienophile molar ratio of 1 : 1 to 4 : 1. The physicochemical constants of the synthesized adducts XVII–XXIII are given in Table 2, and the influence of reaction conditions (temperature, time, reactant ratio) on the adduct yield is illustrated by Table 3.

As seen from Table 3, one of the main parameters affecting the adduct formation rate is temperature. Below 100°C, there is virtually no reaction. With an increase in the temperature from 100 to 160°C, the yield of adduct XX increases from 10 to 82%. With an increase in the diene : dienophile ratio from 1 : 1 to 3 : 1, the yield of adduct XX increases from 52 to 82%. Further increase in the molar ratio to 4 : 1 has virtually no effect on the yield: it increases to only 83%. An increase in the temperature to 180°C leads to a decrease in the yield of adduct XX to 71% and to partial tarring of the reaction mixture.

With propargyl mono-, di- and tribromoacetate as examples, we examined how the number of halogen atoms in dienophile molecules affects the yield of the corresponding adducts XX–XXII. Propargyl monobromo-acetate reacts with hexachlorobutadiene more readily than do propargyl di- and tribromoacetate. The adduct yield at 160°C, reaction time of 12 h, and diene : dienophile molar ratio of 3 : 1 decreases from 82% for XX to 78% for XXI and 61% for XXII. That is, the dienophilic activity decreases with an increase in the number of halogen atoms:

- CH₂Br > CHBr₂ > CBr₃
  - 82% 78% 67%

To determine how the kind of the halogen atoms in the dienophile molecule affects their activity and adduct yield, we compared the reactions of [4+2]-cycloaddition of hexachlorocyclopentadiene to propargyl trihaloacetates XI, XIV, and XV under similar conditions (160°C, 12 h, diene : dienophile molar ratio 3 : 1). As judged from the yields, the compounds can be ranked in the following order:

- CH₂Br > CHBr₂ > CBr₃
  - 82% 78% 67%