Nitrosonium Ion Promoted Iodination and 1,2-Iodofunctionalization of Cyclohexene

Finn Radner

Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden


The promoting influence of NO⁺BF₄⁻ on the addition of I₂ or 'I⁺Nu⁻' couples to cyclohexene (I) in the presence of O₂ is described. 1-Acetoxy-2-iodocyclohexene is obtained in 89% isolated yield from the reaction of I₂, I⁻ and CH₃COOH in CH₂Cl₂, and the corresponding methoxy- and acetamido-substituted iodocyclohexanes are obtained in 96 and 92% yield, when methanol and acetonitrile, respectively, are added. Applications of the method to the synthesis of cis-1,2-cyclohexanediol (Woodward reaction) and bis(2-iodocyclohexyl) ether is described.

The addition of halogens to multiple bonds is one of the fundamental reactions of organic chemistry.¹ However, just as in the case of aromatic halogenation, while the reactions of bromine and chlorine generally are essentially quantitative and simple to perform, those involving iodine are often reversible or otherwise hampered with difficulties. Consequently, the literature on the addition and substitution reactions of chlorine and bromine completely overshadows that of iodine. I recently reported on a convenient method for the iodination of aromatic compounds² which utilized the nitrosonium ion, NO⁺, as a catalyst and O₂ as the stoichiometric oxidant [eqn. (1b)].²

ArH + 0.5 I₂ + ox → ArI + H⁺ + red⁻ (1a)
ArH + I⁻ + H⁺ + 0.5 O₂ → ArI + H₂O (1b)

In this paper the catalytic action of NO⁺ on four reactions involving I₂–alkene interactions are presented, using cyclohexene as the model alkene (Scheme 1). The reactions to be discussed are (a) addition of I₂ [eqn. (2)],³,⁴ (b) 1,2-iodofunctionalization, i.e. the addition of an iodine-nucleophile pair [eqn. (3)],⁴,⁵ (c) preparation of cis-diols (Woodward reaction, [eqn. (4)]),⁵,¹¹ and (d) preparation of bis(2-iodocyclohexyl) ether [eqn. (5)].¹⁵,¹⁷ All of these reactions have been more or less extensively investigated, but the procedures in most cases require the presence of an often expensive oxidizing agent [eqn. (6)] or iodide ion trap [eqn. (7)] as shown below for the iodosfunctionalization reaction. By far the most important feature of the present procedure rests in its demand for no more than a catalytic amount of NO⁺, provided that stoichiometric quantities of O₂ are available.

Results

Addition of I₂ to cyclohexene. Although a number of papers on the iodoniation of alkenes has appeared,¹,⁴ the reaction is of little practical importance.¹⁴ The reaction is promoted by ambient light,³ but unless a very large excess of alkene is used, equilibrium mixtures of the alkene, I₂ and 1,2-diiodo-alkene are obtained. The latter compounds generally revert to the alkene and I₂ when allowed to stand.¹⁵,¹⁴ I now report on the effects of added NO⁺BF₄⁻ on the reaction.

Depending on the concentration of the reactants, the position of the equilibrium I₂ + I⁻ ⇌ 2 in CH₂Cl₂ in the absence of NO⁺BF₄⁻ was in the range of 45–90% conversion of I₂ (Table 1). The addition of a small amount of NO⁺BF₄⁻ caused a decrease in the intensity of the violet color and completely colorless solutions were obtained when the initial concentration of I₂ was low (<0.0010 M) as shown in Table 1. Since the position of an equilibrium cannot be altered by the addition of a catalyst, the effect of NO⁺ must be to effect another reaction pathway, or some-

<table>
<thead>
<tr>
<th>Added NO⁺ b</th>
<th>[I]/M</th>
<th>[I₂]/M</th>
<th>Time/h</th>
<th>Conversion of I₂ into 2(%)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>0.010</td>
<td>0.0010</td>
<td>12</td>
<td>48f</td>
</tr>
<tr>
<td>No</td>
<td>0.200</td>
<td>0.020</td>
<td>12</td>
<td>90</td>
</tr>
<tr>
<td>Yes</td>
<td>0.010</td>
<td>0.0010</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>Yes</td>
<td>0.100</td>
<td>0.010</td>
<td>4</td>
<td>100</td>
</tr>
</tbody>
</table>

* Reactions were performed at 20–23°C in 100 ml of CH₂Cl₂.
* NO⁺BF₄⁻ (5 mol % of the amount of I₂) was added in one portion at the beginning of the reaction. fDetermined spectrophotometrically. gUnchanged after 48 h.

Aromatic iodoniation can be performed in the presence of, e.g., an Ag⁺ salt or a Lewis acid, L, instead of an oxidizing agent [eqn. (1a)], i.e. ArH + I₂ + Ag⁺ → ArH + Ag⁺ + H⁺ or ArH + I₂ + L → ArI + Li⁺ + H⁺. For references, see Ref. 2.

Scheme 1. NO$^+$-promoted iodination of cyclohexene. Nu = OCH$_3$ (3a), OCOCH$_3$ (3b), NHCOCH$_3$ (3c), SCN (3d), OC$_6$H$_5$ (3e), OH (3f), Cl (3g), Br (3h), OCOCF$_3$ (3k).

\[ \text{R} \text{-CH} = \text{CH} \text{-R} + 0.5 \text{I}_2 + \text{Nu}^- \rightarrow \text{RCH(I)CH(Nu)R + red}^- \]  

(6)

\[ \text{R} \text{-CH} = \text{CH} \text{-R} + \text{I}_2 + \text{Ag}^+ + \text{Nu}^- \rightarrow \text{RCH(I)CH(Nu)R + AgI} \]  

(7)

The disappearance of I$_2$ was of an autocatalytic, albeit sluggish, nature as shown in Fig. 1, and the product of this NO$^+$-promoted reaction was mainly 2. Due to the instability of 2 toward work-up, GLC analysis, etc., no detailed investigation could be performed to ascertain whether all of the I$_2$ was converted into 2, or whether some I$_2$ was lost in reactions with reagents other than 1 or with 1 to yield products other than 2.

When the excess of 1 was decreased from 10:1 to 1.5:1, incomplete decolorization generally resulted, also in the

---

*Fig. 1. Plot of formation of 1,2-diiodocyclohexane (2), vs. time in the presence and absence of NO$^+$BF$_4^-$; [1] = 0.010 M, [I$_2$] = 0.0010 M, [NO$^+$BF$_4^-$] = 0 (squares) or 0.00010 M (circles). The filled and open circles represent the results from two identically performed runs.*
Table 2. 1,2-Iodofunctionalization of cyclohexene (1) in CH$_2$Cl$_2$. [I$_2$] = 0.20 M, [nucleophile] = 0.50 M, [NO$_2$BF$_4$] = 0.005 M.*

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Product</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>3a</td>
<td>96</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>3b</td>
<td>89</td>
</tr>
<tr>
<td>CH$_3$CN$^a$</td>
<td>3c</td>
<td>&lt;30$^a$</td>
</tr>
<tr>
<td>CH$_3$CN/H$_2$O$^b$</td>
<td>3d</td>
<td>92</td>
</tr>
<tr>
<td>NaSCN$^a$</td>
<td>3d</td>
<td>52</td>
</tr>
<tr>
<td>C$_2$H$_4$OH</td>
<td>3e</td>
<td>41</td>
</tr>
</tbody>
</table>

*Reactions at 25°C in 200 ml of CH$_2$Cl$_2$ for 16 h in Erlenmeyer flasks equipped with drying tubes. $^a$Solvent = CH$_3$CN. $^b$Solvent = CH$_3$CN with H$_2$O (0.20 M) added. $^c$(C$_2$H$_5$)$_2$NSCN (0.020 M) was added. $^d$See the text and Experimental section.

presence of NO$_2$BF$_4$$. At higher concentrations of I$_2$ ([I$_2$] >0.020 M) in CH$_2$Cl$_2$, and with a 10:1 excess of I, the NO$_2$-catalyzed reaction gave colored reaction products. Commonly, intensely blue solutions ($	ext{d}_{	ext{max}} = 602$ nm) resulted and these turned orange-brown on addition of water. The main product was 2 but the formation of by-products, among them 3h after work-up, severely limits the preparative usefulness of the method.

1,2-Iodofunctionalization of cyclohexene. The addition of an ‘1‘Nu$^-$’ couple [eqn. (3)] across the multiple bonds of alkenes, alkynes and dienes has gained considerable interest over many years.$^b$ The most common reagents are different I$_2$/Ag$^+$, Hg$^{11+}$ or Ti$^4+$-salt/nucleophile combinations,$^b$ but a variety of other reagents is available, especially for the introduction of ‘1‘RCOO$^-$’ as in the Prevost and Woodward reactions.$^-$ Barluenga recently described the introduction of a number of nucleophiles$^a$ by the reaction of HgO·HBF$_4$ with I$_2$/pyridine followed by addition of the alkene, a nucleophile source and HBF$_4$.$^{12}$ The procedures generally require promotion by a stoichiometric amount of an iodide-precipitating agent [eqn. (7)] or an oxidizing agent (e.g. [eqn. (6)], Pb(OCOCH$_3$)$_2$, CH$_3$COOH$^+$ or KIO$_3$).$^{16}$ However, addition of ‘1‘OR$^-$ (R = H, CH$_3$, COCH$_3$) proceeds in CHCl$_3$sulfolane without added promoting agent$^{14}$ and catalysis by nitrous acid has been observed in the O$_2$-promoted addition of ‘1‘OR$^-$ in aqueous dioxane.$^{15}$

In the present study, a mixture of I$_2$, I and a nucleophile source (molar ratio 1.3:1:0.2:2.5) in CH$_2$Cl$_2$ was treated with a catalytic (1–5 mol%) amount of NO$_2$BF$_4$ in the presence of air or oxygen (Table 2). The reactions were monitored by GLC and overnight treatment was generally sufficient for complete consumption of I on the 40 mmol scale, when the nucleophile source was readily soluble in CH$_2$Cl$_2$. After work-up, colorless (3a, 3d) or slightly orange (3b) oils were obtained.

When the reaction was performed in CH$_3$CN in the absence of any other nucleophile, a brown oil corresponding to ca. 30% of the initial amount of I resulted. On addition of an equimolar (to I) amount of H$_2$O, excellent yields of the acetylamidated product 3c were collected as colorless crystals after work-up. The use of inorganic salts as sources of nucleophiles was more efficient in CH$_3$CN than in CH$_2$Cl$_2$ but the formation of 3e interfered. Hence the reaction was considered inferior to other methods for the synthesis of, e.g. bromo- or chloro-substituted iodoalkanes.$^-$ Introduction of the SCN group could be achieved in CH$_2$Cl$_2$ in the presence of tetra-alkyllammonium salts, but more convenient routes to 3e are already available.$^b$ Addition of ‘1‘CF$_2$COO$^-$’ could be achieved in a manner similar to that for iodoacetoxyluation, but addition of ‘H‘CF$_2$COO$^-$’ interfered and sometimes dominated the reaction. When H$_2$O was used as the nucleophile source in experiments similar to those in Table 1, incomplete conversion of I resulted, giving only low yields of the iodohydrin 3f.

In order to quantify the catalytic action of NO$_2$BF$_4$, the experiments summarized in Table 3 were performed. Obviously, iodomethoxylation also takes place in the absence of NO$_2$BF$_4$ and O$_2$ yielding an equilibrium mixture of 1, 1 and 3a in accordance with earlier reports.$^{16}$ NO$_2$/O$_2$ apparently acts by effecting a pathway other than through this equilibrium since almost complete conversion of I into 3a was observed.

The Woodward reaction. The Woodward method for the synthesis of cis-diols results in overall syn addition from the more hindered side of the alkene,$^{16}$ and has been the subject of numerous investigations aimed at finding replacements for the silver acetate used in the original proc...

Table 3. Iodomethoxylation of cyclohexene under different conditions in CH$_2$Cl$_2$. [I$_2$] = 0.20 M, [I] = 0.23 M, [CH$_3$OH] = 0.50 M.

<table>
<thead>
<tr>
<th>[NO$_2$] / M</th>
<th>Atmosphere$^6$</th>
<th>Yield (%)$^6$ after 2 h</th>
<th>16 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>O$_2$</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>0.005</td>
<td>Ar</td>
<td>30</td>
<td>54</td>
</tr>
<tr>
<td>0</td>
<td>Ar</td>
<td>18</td>
<td>42</td>
</tr>
<tr>
<td>0.005</td>
<td>Air</td>
<td>96</td>
<td>97</td>
</tr>
</tbody>
</table>

*Reactions performed with magnetic stirring in 80 ml of CH$_2$Cl$_2$ at 20–23°C. $^a$A small, constant overpressure of O$_2$ or Ar or air was furnished via a drying tube. $^b$Determined by GLC.
dure.\textsuperscript{5-11} When the iodoacetylated product 3b obtained in the previous section was subjected to solvolysis with CH\textsubscript{3}COOH/CH\textsubscript{3}COOH followed by alkaline hydrolysis, cis-1,2-cyclohexanediol (4) was obtained in 78\% isolated yield. In comparison, the yields obtained with CH\textsubscript{3}COOH\textsubscript{3} KIO\textsubscript{3},\textsuperscript{10} and (CH\textsubscript{3}COO)\textsubscript{2}Cu\textsuperscript{11} were 86, 75 and 83\%, respectively.

**Preparation of bis(2-iodocyclohexyl) ether.** When alkenes are treated with sources of iodine oxide, formation of bis(2-iodoalkyl) ethers may result.\textsuperscript{15-17} Thus 5a was obtained in 23\% yield when 1 was treated with HgO/I\textsubscript{2} in CCl\textsubscript{4},\textsuperscript{16} and as a minor product when 1 was treated with an ozonised solution of I\textsubscript{2}.\textsuperscript{17} When I\textsubscript{2} and 1 were exposed O\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2} with no nucleophile added, the only reaction observed was formation of the diiodide 2. However, if a second portion of NO\textsuperscript{+}BF\textsubscript{4}\textsuperscript{-} was added, conversion into 5a slowly occurred. In a typical run, 1 (0.050 mol), I\textsubscript{2} (0.020 mol) and NO\textsuperscript{+}BF\textsubscript{4}\textsuperscript{-} (2 × 0.001 mol) were added, and after the reaction had been stirred for 48 h, 5a could be isolated in 78\% yield based on 1. In another experiment, 1 (0.120 mol) and excess I\textsubscript{2} (0.067 mol) were stirred under O\textsubscript{2} and NO\textsuperscript{+}BF\textsubscript{4}\textsuperscript{-} (4 × 0.001 mol) was added every 48 h. After 7 days, 5a (0.052 mol, 87\%) was isolated as a colorless oil. Obviously the reaction follows the stoichiometry of eqn. (9). In addition to spectral and analytical data, the identity of 5a was established by its conversion into dicyclohexyl ether

\[
2 \text{I}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}^+ \rightarrow 5a
\]  

(5b) upon treatment with (C\textsubscript{6}H\textsubscript{5})\textsubscript{3}SnH and conversion into bis(3-cyclohexenyl) ether (5c) when refluxed with Na\textsubscript{2}S in 1-propanol.

**Formation of 3-substituted cyclohexenes.** The initial experiments on the iodo-methoxylation and -acetoxylation reaction were performed with excess I\textsubscript{2} in CH\textsubscript{2}CN which created some confusion. Complex product mixtures resulted containing: (a) the diiodide 2 which slowly reverted to starting materials resulting in continuous violet coloration; (b) the iodo-functionalized product 3a or 3b; (c) the iodoacetamidated product 3d which was not analyzable under the GLC conditions employed, and finally (d) about 6–11\% of some other products, to which this last section will be devoted.

The compounds were shown by MS and NMR to be the products of overall allylic substitution (6a-c). When 1 was treated with CH\textsubscript{3}COOH/CH\textsubscript{3}CN and NO\textsuperscript{+}BF\textsubscript{4}\textsuperscript{-} in the absence as well as in the presence of a small amount of I\textsubscript{2}, 6a and 6b were formed in similar quantities as observed above (9–11\% and 1\% yield based on 1, respectively). The yields of 6a + 6c based on NO\textsuperscript{+} were generally > 100\% but a detailed study on the possibly catalytic nature of this reaction is beyond the scope of the present investigation. With CH\textsubscript{3}OH/CH\textsubscript{3}CN similar results were obtained; 6–9\% of 6b and 1\% of 6c were formed. All attempts to raise the yields of 6a–6c have so far been unsuccessful, but will be the subject of future investigation. For this study the most important finding is that the seriousness of these reactions as undesired side-reactions to the iodo-functionalization reaction was much less pronounced in CH\textsubscript{2}Cl\textsubscript{2} than in CH\textsubscript{3}CN; generally 0–3\% of allylically substituted products were formed in the reactions of Table 1.

**Discussion**

The additon of I\textsubscript{2} to double bonds is complicated by the possibility of a light-catalyzed radical pathway as well as a ‘dark’, probably electrophilic, pathway. The first pathway has been suggested to involve attack by an iodine atom on an alkene–I\textsubscript{2} charge-transfer complex, while the latter initially probably yields a cyclic iodonium ion [eqn. (10)]. The

\[
\text{O} \quad \text{O} \quad \text{I} \\
-\text{C}=\text{C}^- + \text{I}^+ \rightleftharpoons -\text{C}^\cdot =\text{C}^- 
\]  (10)

\[
\text{O} \quad \text{O} \quad \text{I} \\
-\text{C}=\text{C}^- + \text{I}^- \rightleftharpoons -\text{C}=\text{C}^- + \text{I}_2 + \text{I}^- 
\]  (11)

reversion of the diiodide into starting material may also proceed via either an ion or an iodine-atom catalyzed pathway [eqn. (11)]. Since both of these pathways will, or at least in principle can, contribute to the overall reaction, the observed position of the equilibrium 1 + I\textsubscript{2} ⇌ 2 will be sensitive to the experimental conditions, in accordance with the discrepancies in the data found in the literature. In the absence of e.g. kinetic data and knowledge of the
behaviour of other alkenes* the mechanistic speculations presented here necessarily must be kept fairly prudent. The following suggestions do however seem appropriate.

1,2-Diodopentane has been reported to be reasonably stable in the dark in the absence of traces of I₂.¹¹ In solution, the diiodide 2 slowly underwent conversion into I₂ and 1, to yield equilibrium mixtures of 1 and 2. On the other hand, the reaction mixtures resulting from the NO⁺-promoted reactions of Table 1 remained colorless for >1 week prior to work-up, i.e. in the presence of NO⁺. One fundamental difference between NO⁺-promoted aromatic iodination and the reactions presented here is that while essentially no iodoaromatic compounds were formed in the absence of NO⁺/O₂,² significant formation of 2 as well as of 3a–3c resulted without NO⁺ (Tables 2 and 3). This suggests that the role of NO⁺ is to promote the formation of some positive iodine species [eqn. (12)] as in

\[ I⁻ + NO⁺BF₄⁻ \rightarrow \text{I}⁺⁺BF₄⁻ + INO \] (12a)

\[ 2 \text{INO} \rightarrow I₂ + 2 NO \xrightarrow{\text{O}_2} \rightarrow \text{NO}⁺ \] (12b)

aromatic iodination,² and in the case of the I⁺-addition reaction also to inhibit the I-atom catalyzed decomposition of 2 [eqn. (11)], possibly by minimizing the concentration of free iodine atoms. One possibility, assuming that the induction period of Fig. 1 is due to the build-up of a sufficiently high concentration of NO⁺,¹ is that the apparently autocatalytic reaction in Fig. 1 is rather ‘autoxantinhibited’ (i.e., the reverse reaction is more efficiently inhibited towards the end of the forward reaction) by the capture of the iodine atoms by NO or INO [eqn. (13)].

I + NO \rightarrow INO \] (13a)

I + INO \rightarrow I₂ + NO \] (13b)

The role of NO⁺ in the iodofunctionalization reaction is to speed up and complete the formation of I⁺⁺ [eqn. (12)]. The iodofunctionalized product probably results by capture of the iodonium ion [eqn. (10)] by the nucleophile present.³ The formation of diiododalkyl ethers has been examined and suggested to be the result of oxidation of I₂ to IO followed by addition of I⁺⁺ to I⁻⁻. The excellent yields obtained result from the absence of concurrent (OF⁻) nucleophiles. The formation of the allylically substituted side products will be the subject of a separate investigation and at the present stage only two possible modes of action will be mentioned; abstraction of an allylic hydrogen⁶ (to yield NOH) or allylic oxidation⁶ (to yield NO).

**Experimental**

*Materials and methods.* Dichloromethane and acetonitrile (Merck zur Rückstandsanalyse) were dried and stored over 3 Å molecular sieves. Other solvents were of analytical grade and used as supplied. Cyclohexene (Riedel, 99%), nitrosonium tetrafluoroborate (Merck) and iodine (Merck) were used without further purification. All other reagents were of highest purity available and used as supplied.

Column chromatography was performed on 20×70 mm columns on silica gel 60 (Merck, 230–400 mesh). GLC analyses were performed on 25 m×0.2 mm OV-1701 on a Varian 3400 gas chromatograph equipped with a Varian 4270 integrator or on 3 m×3 mm OV-101 on Chromosorb W on an HP 5308A gas chromatograph equipped with an HP 18850A integrator. ¹H and ¹³C NMR and mass spectra were recorded as previously described,² and all compounds had satisfactory spectral data. UV/VIS spectra were recorded on a Cary 219 spectrophotometer.

**Addition of I₂ to 1.** Appropriate (Table 1 and Fig. 1) amounts of 1 in CH₂Cl₂ were added to solutions of I₂ in CH₂Cl₂, and the required amount of NO⁺BF₄⁻ was added. Aliquots were withdrawn at intervals (ca. 5 min) and the concentration of I₂ was determined spectrophotometrically. After work-up (washing with water, aq. Na₂S₂O₅, water, drying and evaporation) 2 could be obtained as a slightly brownish oil which liberated I₂ when allowed to stand.

**1,2-Iodofunctionalization of 1.** (a) *Iodomethoxylation.* A mixture of I₂ (0.050 mol), 1 (0.040 mol), CH₂OH (0.100 mol) and NO⁺BF₄⁻ (0.0008 mol) in 200 ml of CH₂Cl₂ was stirred under O₂ for 16 h. The mixture was washed with water, aq. Na₂S₂O₅ and water, dried and evaporated, and the resulting brown oil was chromatographed (pentane–diethyl ether 10:1) to yield 3a (0.039 mol, 96%) as a colorless oil.

(b) *Iodoacetoxylation.* Replacement of CH₂OH with CH₃COOH yielded, after chromatography, 3b (0.036 mol, 89%) as a slightly orange oil, >99 % pure by GLC.

(c) *Iodoacetalidation.* A mixture of I₂ (0.050 mol), 1 (0.040 mol), H₂O (0.040 mol) and NO⁺BF₄⁻ (0.0008 mol) in 200 ml CH₂CN was stirred for 16 h, exposed to ambient air via a drying tube. 300 ml of CH₂Cl₂ were added and after work-up as described under (a), 3c (0.037 mol, 92%) was collected as colorless crystals, m.p. 121–123°C (CCl₄).

(d) *Iodothiocyanation.* Replacement of CH₂OH with NaSCN (0.100 mol) and (C₆H₅)₂NCSN (0.003 mol) yielded 3d (0.021 mol, 52%) as a colorless oil.

**Preparation of cis-cyclohexane-1,2-diol (4).** A mixture of 1 (0.050 mol), 1 (0.040 mol), CH₂COOH (0.100 mol) and

---

* Preliminary investigations show that 2-pentene and 1-octene are suitable as substrates in the iodomethoxylation reaction and for the preparation of diiododalkyl ethers.

¹ Under the reaction conditions utilized (see Fig. 1) the second step of eqn. (12b) is not possible.
NO\cdot BF\textsubscript{4}\textsuperscript{-} (0.0008 mol) was stirred for 40 h, exposed to ambient air via a drying tube. After 16 h, a second portion of NO\cdot BF\textsubscript{4}\textsuperscript{-} was added to ensure complete conversion. After work-up (column chromatography omitted), a pale brown liquid resulted, which was refluxed with CH\textsubscript{3}COOK (0.040 mol) in 150 ml of CH\textsubscript{3}COOH for 16 h. After addition of H\textsubscript{2}O/CH\textsubscript{3}Cl\textsubscript{2}, washing of the organic layer with H\textsubscript{2}O, aq. Na\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}O and drying, a pale brown crystalline mass was obtained after evaporation [\textgt{95\% cis-diacetoxy cyclohexene (GLC)]. The crude mass was dissolved in 200 ml of benzene and treated with 15 g of KOH in 150 ml of CH\textsubscript{3}OH under reflux for 2 h. 20 ml of H\textsubscript{2}O were added and the reaction product obtained after evaporation was extracted with 6x100 ml of CH\textsubscript{2}Cl\textsubscript{2}, dried, evaporated and recrystallized from CCl\textsubscript{4} to yield 4 (0.031 mol, 78\%) as colorless crystals, m.p. 96–98\degree C.

Preparation of bis(2-iodocyclohexyl) ether (5a). A mixture of I\textsubscript{2} (0.067 mol), I\textsubscript{1} (0.120 mol), and NO\cdot BF\textsubscript{4}\textsuperscript{-} (0.001 mol) in 300 ml of CH\textsubscript{3}Cl\textsubscript{2} was stirred under O\textsubscript{2} for 7 days and additional portions of NO\cdot BF\textsubscript{4}\textsuperscript{-} (0.001 mol) were added on days 2, 4 and 6. At this stage, no 1 remained according to GLC. After work-up as described for 3a above, 5a (0.047 mol, 78\%) could be obtained as a colorless oil.

Reaction of 5a with (C\textsubscript{6}H\textsubscript{5})\textsubscript{3}SnH and Na\textsubscript{2}S. 5a (0.0092 mol) and (C\textsubscript{6}H\textsubscript{5})\textsubscript{3}SnH (0.020 mol) were heated for 2 h and the resulting mixture was subjected to chromatography with toluene as the eluent. After rejection of the first ca. 100 ml, 0.060 mol (65\%) of a colorless oil was collected from the following fractions, identified as dicyclohexyl ether (5h). When 5a (0.016 mol) and Na\textsubscript{2}S (0.090 mol) were refluxed in 70 ml of n-C\textsubscript{6}H\textsubscript{14}OH, bis(3-cyclohexenyl) ether (5c, 0.015 mol, 96\%) was obtained as a colorless oil after addition of CH\textsubscript{2}Cl\textsubscript{2}/H\textsubscript{2}O, washing, drying, evaporation and chromatography.

Formation of 3-substituted cyclohexenes. When the iodo-functionalization reactions presented above were performed in CH\textsubscript{3}CN, a set of by-products was invariably formed. Their mass spectra were in accordance with structures 6a–6c. When 1 (0.040 mol) and NO\cdot BF\textsubscript{4}\textsuperscript{-} (0.0008 mol) were stirred under O\textsubscript{2} in 40 ml of CH\textsubscript{3}COOH and 15 ml of CH\textsubscript{3}CN in the presence, as well as in the absence, of I\textsubscript{2} (0.001 mol), 6a (0.004 mol) and 6c (0.0004 mol) were formed as determined by GLC. From runs on a larger scale 6a, 6b and 6c, respectively, were isolated and identified by \textsuperscript{1}H and \textsuperscript{13}NMR spectroscopy, 6c as a mixture of two diastereomeric forms.

Acknowledgements. I thank Dr. Mats Malmberg for help with the NMR spectra, Professor Lennart Eberson for helpful comments and the Swedish Natural Science Research Council for financial support.

References


Received May 19, 1989.