

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

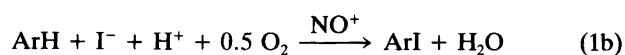
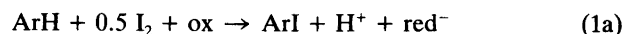
Finn Radner

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

Radner, F., 1989. Nitrosonium Ion Promoted Iodination and 1,2-Iodofunctionalization of Cyclohexene. – Acta Chem. Scand. 43: 902–907.

The promoting influence of NO^+BF_4^- on the addition of I_2 or 'I⁺Nu⁻' couples to cyclohexene (**1**) in the presence of O_2 is described. 1-Acetoxy-2-iodocyclohexane is obtained in 89 % isolated yield from the reaction of I_2 , **1** and CH_3COOH in CH_2Cl_2 , 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.^{1a} 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 compounds* which utilized the nitrosonium ion, NO^+ , as a catalyst and O_2 as the stoichiometric oxidant [eqn. (1b)].²



In this paper the catalytic action of NO^+ on four reactions involving I_2 -alkene interactions are presented, using cyclohexene as the model alkene (Scheme 1). The reactions to be discussed are (a) addition of I_2 [eqn. (2)],^{3,4} (b) 1,2-iodofunctionalization, i.e. the addition of an iodine-nucleophile pair [eqn. (3)],⁴⁻¹⁵ (c) preparation of *cis*-diols (Woodward reaction, [eqn. (4)]),³⁻¹¹ 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 iodofunctionalization 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 O_2 are available.

Results

Addition of I_2 to cyclohexene. Although a number of papers on the iodination of alkenes has appeared,^{3,4} the reaction is of little practical importance.^{1a} The reaction is promoted by ambient light,³ but unless a very large excess of alkene is used, equilibrium mixtures of the alkene, I_2 and 1,2-diiodo-alkene are obtained. The latter compounds generally revert to the alkene and I_2 when allowed to stand.^{1a,4} I now report on the effects of added NO^+BF_4^- on the reaction.

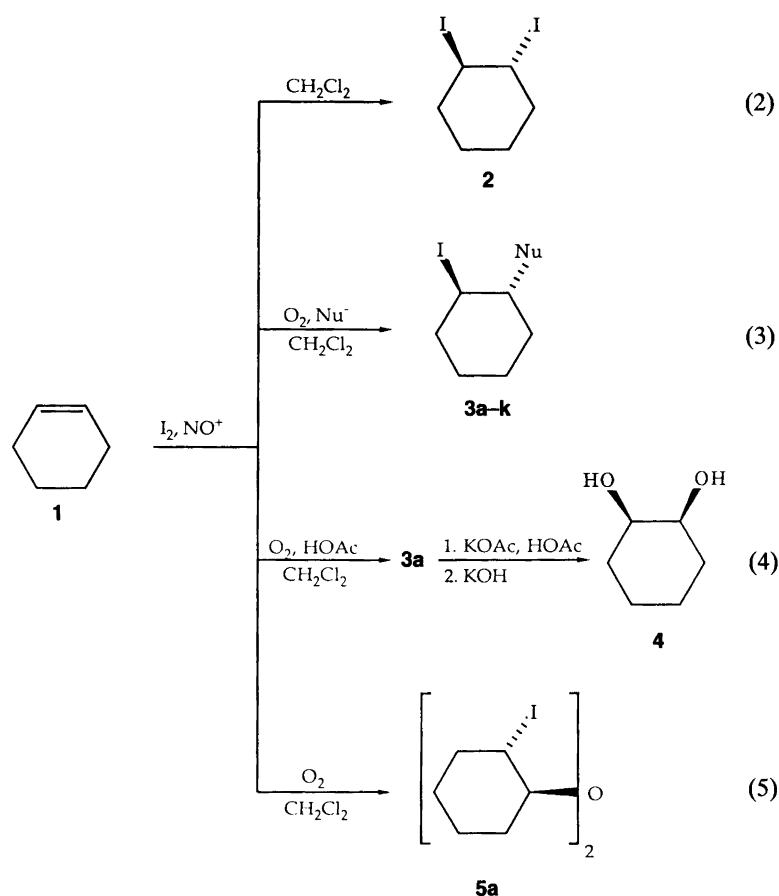
Depending on the concentration of the reactants, the position of the equilibrium $\text{I}_2 + \mathbf{1} \rightleftharpoons \mathbf{2}$ in CH_2Cl_2 in the absence of NO^+BF_4^- was in the range of 45–90 % conversion of I_2 (Table 1). The addition of a small amount of NO^+BF_4^- caused a decrease in the intensity of the violet color and completely colorless solutions were obtained when the initial concentration of I_2 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 1. Reaction of cyclohexene (**1**) and I_2 in CH_2Cl_2 .^a

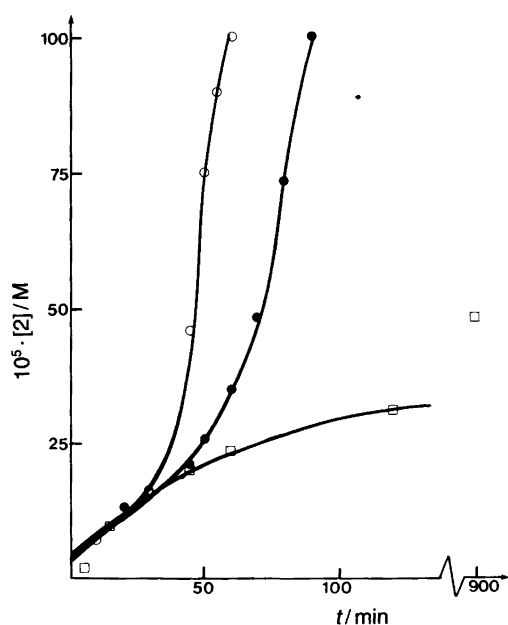
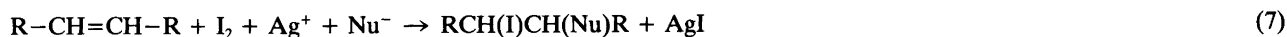
Added NO^+ ^b	[1]/M	[I_2]/M	Time/h	Conversion of I_2 into 2 (%) ^c
No	0.010	0.0010	12	48 ^d
No	0.200	0.020	12	90
Yes	0.010	0.0010	1	100
Yes	0.100	0.010	4	100

* Aromatic iodination 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. $\text{ArH} + \text{I}_2 + \text{Ag}^+ \rightarrow \text{ArI} + \text{AgI} + \text{H}^+$ or $\text{ArH} + \text{I}_2 + \text{L} \rightarrow \text{ArI} + \text{LI} + \text{H}^+$. For references, see Ref. 2.

^aReactions were performed at 20–23 °C in 100 ml of CH_2Cl_2 .
^b NO^+BF_4^- (5 mol % of the amount of I_2) was added in one portion at the beginning of the reaction. ^cDetermined spectrophotometrically. ^dUnchanged after 48 h.



Scheme 1. NO^+ -promoted iodination of cyclohexene. Nu = OCH_3 (**3a**), OCOCH_3 (**3b**), NHCOCH_3 (**3c**), SCN (**3d**), OC_4H_9 (**3e**), OH (**3f**), Cl (**3g**), Br (**3h**), OCOCF_3 (**3k**).



how alter the mode of consumption of I_2 . 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-diodocyclohexane (**2**), vs. time in the presence and absence of NO^+BF_4^- . $[\text{1}] = 0.010 \text{ M}$, $[\text{I}_2] = 0.0010 \text{ M}$, $[\text{NO}^+\text{BF}_4^-] = 0$ (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 CH₂Cl₂. [1] = 0.20 M, [I₂] = 0.25 M, [nucleophile] = 0.50 M, [NO⁺BF₄⁻] = 0.005 M.^a

Nucleophile	Product	Isolated yield (%)
CH ₃ OH	3a	96
CH ₃ COOH	3b	89
CH ₃ CN ^b	3c	<30 ^e
CH ₃ CN/H ₂ O ^c	3c	92
NaSCN ^d	3d	52
C ₄ H ₉ OH	3e	41

^aReactions at 25 °C in 200 ml of CH₂Cl₂ for 16 h in Erlenmeyer flasks equipped with drying tubes. ^bSolvent = CH₃CN. ^cSolvent = CH₃CN with H₂O (0.20 M) added. ^d(C₄H₉)₄NSCN (0.020 M) was added. ^eSee the text and Experimental section.

presence of NO⁺BF₄⁻. At higher concentrations of I₂ ([I₂] > 0.020 M) in CH₂Cl₂, and with a 10:1 excess of **1**, the NO⁺-catalyzed reaction gave colored reaction products. Commonly, intensely blue solutions (λ_{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 I⁺Nu⁻ couple [eqn. (3)] across the multiple bonds of alkenes, alkynes and dienes has gained considerable interest over many years.^{1b} The most common reagents are different I₂/Ag⁺, Hg²⁺- or Tl⁺-salt/nucleophile combinations,⁵⁻⁷ but a variety of other reagents is available, especially for the introduction of 'I⁺RCOO⁻' as in the Prevost and Woodward reactions.⁸⁻¹¹ Barluenga recently described the introduction of a number of nucleophiles* by the reaction of HgO · HBF₄ with I₂/pyridine followed by addition of the alkene, a nucleophile source and HBF₄.¹² 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(OCOCH₃)₄,⁸ CH₃COOOH⁹ or KIO₃).¹⁰ However, addition of I⁺OR⁻ (R = H, CH₃, COCH₃) proceeds in CHCl₃/sulfolane without added promoting agent¹⁴ and catalysis by nitrous acid has been observed in the O₂-promoted addition of I⁺OR⁻ in aqueous dioxane.¹⁵

In the present study, a mixture of I₂, **1** and a nucleophile source (molar ratio 1.3:1.0:2.5) in CH₂Cl₂ was treated with a catalytic (1–5 mol %) amount of NO⁺BF₄⁻ 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 **1** on the 40 mmol scale, when the nucleophile source was readily soluble in

* The following Nu⁻ parts of the corresponding I⁺Nu⁻ couples were introduced: F⁻, Cl⁻, Br⁻, NO₂⁻, OCN⁻, OH⁻, CH₃COO⁻, CH₃O⁻, H⁻, C₆H₅⁻, CH₃CONH⁻. Similar results were obtained with CuO · HBF₄.¹³

Table 3. Iodomethoxylation of cyclohexene under different conditions in CH₂Cl₂. [1] = 0.20 M, [I₂] = 0.23 M, [CH₃OH] = 0.50 M.

[NO ⁺]/M	Atmosphere ^b	Yield (%) ^c after	
		2 h	16 h
0.005	O ₂	98	98
0.005	Ar	30	54
0	Ar	18	42
0.005	Air	96	97

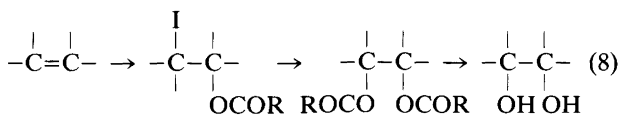
^aReactions performed with magnetic stirring in 80 ml of CH₂Cl₂ at 20–23 °C. ^bA small, constant overpressure of O₂ and Ar or air furnished via a drying tube. ^cDetermined by GLC.

CH₂Cl₂. After work-up, colorless (**3a**, **3d**) or slightly orange (**3b**) oils were obtained.

When the reaction was performed in CH₃CN in the absence of any other nucleophile, a brown oil corresponding to ca. 30 % of the initial amount of **1** resulted. On addition of an equimolar (to **1**) amount of H₂O, excellent yields of the acetamidated product **3c** were collected as colorless crystals after work-up. The use of inorganic salts as sources of nucleophiles was more efficient in CH₃CN than in CH₂Cl₂ but the formation of **3c** interfered. Hence the reaction was considered inferior to other methods for the synthesis of, e.g. bromo- or chloro-substituted iodoalkanes.⁴⁻⁷ Introduction of the SCN group could be achieved in CH₂Cl₂ in the presence of tetra-alkylammonium salts, but more convenient routes to **3e** are already available.⁴ Addition of 'I⁺CF₃COO⁻' could be achieved in a manner similar to that for iodoacetoxylation, but addition of 'H⁺CF₃COO⁻' interfered and sometimes dominated the reaction. When H₂O was used as the nucleophile source in experiments similar to those in Table 1, incomplete conversion of **1** resulted, giving only low yields of the iodohydrin **3f**.

In order to quantify the catalytic action of NO⁺BF₄⁻ the experiments summarized in Table 3 were performed. Obviously, iodomethoxylation also takes place in the absence of NO⁺BF₄⁻ and O₂ yielding an equilibrium mixture of **1**, I₂ and **3a** in accordance with earlier reports.¹⁴ NO⁺/O₂ apparently acts by effecting a pathway other than through this equilibrium since almost complete conversion of I₂ 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,^{1b} and has been the subject of numerous investigations aimed at finding replacements for the silver acetate used in the original proce-

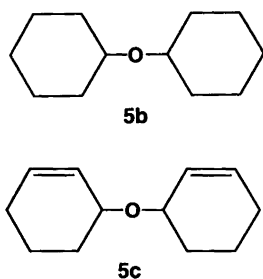


ture.⁵⁻¹¹ When the iodoacetoxylated product **3b** obtained in the previous section was subjected to solvolysis with $\text{CH}_3\text{COOK}/\text{CH}_3\text{COOH}$ followed by alkaline hydrolysis, *cis*-1,2-cyclohexanediol (**4**) was obtained in 78 % isolated yield. In comparison, the yields obtained with CH_3COOTl ,⁵ KIO_3 ,¹⁰ and $(\text{CH}_3\text{COO})_2\text{Cu}$ ¹¹ were 86, 75 and 83 %, respectively.

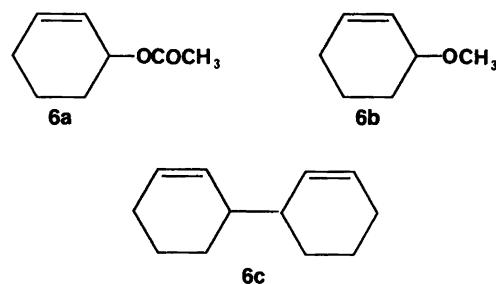
Preparation of bis(2-iodocyclohexyl) ether. When alkenes are treated with sources of iodine oxide, formation of bis(2-iodoalkyl) ethers may result.¹⁵⁻¹⁷ Thus **5a** was obtained in 23 % yield when **1** was treated with HgO/I_2 in CCl_4 ,¹⁶ and as a minor product when **1** was treated with an ozonised solution of I_2 .¹⁷ When I_2 and **1** were exposed O_2 in CH_2Cl_2 with no nucleophile added, the only reaction observed was formation of the diiodide **2**. However, if a second portion of NO^+BF_4^- was added, conversion into **5a** slowly occurred. In a typical run, **1** (0.050 mol), I_2 (0.020 mol) and NO^+BF_4^- (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 I_2 . In another experiment, **1** (0.120 mol) and excess I_2 (0.067 mol) were stirred under O_2 and NO^+BF_4^- (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



(**5b**) upon treatment with $(\text{C}_4\text{H}_9)_3\text{SnH}$ and conversion into bis(3-cyclohexenyl) ether (**5c**) when refluxed with Na_2S in 1-propanol.



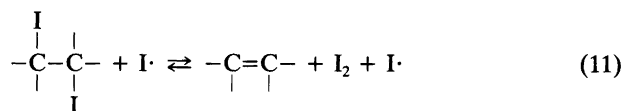
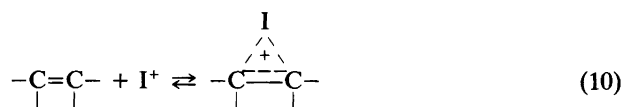
Formation of 3-substituted cyclohexenes. The initial experiments on the iodo-methoxylation and -acetoxylation reaction were performed with excess **1** in CH_3CN which created some confusion. Complex product mixtures resulted containing: (a) the diiodide **2** which slowly reverted to starting materials resulting in continuous violet coloration; (b) the iodofunctionalized 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 $\text{CH}_3\text{COOH}/\text{CH}_3\text{CN}$ and NO^+BF_4^- in the absence as well as in the presence of a small amount of I_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^+ were generally > 100 % but a detailed study on the possibly catalytic nature of this reaction is beyond the scope of the present investigation. With $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ similar results were obtained; 6-9 % of **6b** and 1 % of **6c** were formed. All attempts to raise the yields of **6a-c** 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 iodofunctionalization reaction was much less pronounced in CH_2Cl_2 than in CH_3CN ; generally 0-3 % of allylically substituted products were formed in the reactions of Table 1.

Discussion

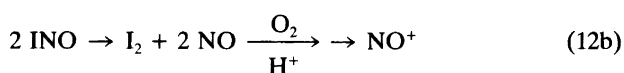
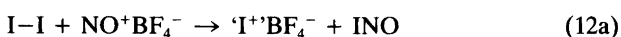
The addition of I_2 to double bonds is complicated by the possibility of a light-catalyzed radical pathway as well as a 'dark', probably electrophilic, pathway. The first pathway has been suggested to involve attack by an iodine atom on an alkene- I_2 charge-transfer complex, while the latter initially probably yields a cyclic iodonium ion [eqn. (10)]. The



reversion of the diiodide into starting material may also proceed via either an ionic 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 $\mathbf{1} + \text{I}_2 \rightleftharpoons \mathbf{2}$ 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-Diiodopentane has been reported to be reasonably stable in the dark in the absence of traces of I_2 .^{3d} In solution, the diiodide **2** slowly underwent conversion into I_2 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^+/O_2 ,² significant formation of **2** as well as of **3a–3c** resulted without NO^+ (Tables 2 and 3). This suggests that the key role of NO^+ is to promote the formation of some positive iodine species [eqn. (12)] as in



aromatic iodination,² and in the case of the I_2 -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 ,[†] is that the apparently autocatalytic reaction in Fig. 1 is rather 'autoantihhibited' (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)].



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.⁹ The formation of diiododialkyl ethers has been examined and suggested to be the result of oxidation of I_2 to I_2O followed by addition of I^+OI^- and subsequent reactions.^{16,17} The role of NO^+ in the system presented here is probably to catalyze the formation of I_2O from I_2 and O_2 . The excellent yields obtained result from the absence of concurrent (OI^-) nucleophiles. The formation of the allylically substituted side products will be the subject of a separate investigation and at the present stage only two

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

[†] Under the reaction conditions utilized (see Fig. 1) the second step of eqn. (12b) is not possible.

possible modes of action will be mentioned; abstraction of an allylic hydrogen¹⁸ (to yield NOH) or allylic oxidation¹⁹ (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%), nitronium 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 20×700 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 I_2 to **1.** Appropriate (Table 1 and Fig. 1) amounts of **1** in CH_2Cl_2 were added to solutions of I_2 in CH_2Cl_2 , and the required amount of $NO^+BF_4^-$ was added. Aliquots were withdrawn at intervals (ca. 5 min) and the concentration of I_2 was determined spectrophotometrically. After work-up (washing with water, aq. $Na_2S_2O_3$, water, drying and evaporation) **2** could be obtained as a slightly brownish oil which liberated I_2 when allowed to stand.

1,2-Iodofunctionalization of **1.** (a) *Iodomethoxylation.* A mixture of I_2 (0.050 mol), **1** (0.040 mol), CH_3OH (0.100 mol) and $NO^+BF_4^-$ (0.0008 mol) in 200 ml of CH_2Cl_2 was stirred under O_2 for 16 h. The mixture was washed with water, aq. $Na_2S_2O_3$ 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 CH_3OH with CH_3COOH yielded, after chromatography, **3b** (0.036 mol, 89%) as a slightly orange oil, >99% pure by GLC.

(c) *Iodoacetamidation.* A mixture of I_2 (0.050 mol), **1** (0.040 mol), H_2O (0.040 mol) and $NO^+BF_4^-$ (0.0008 mol) in 200 ml CH_3CN was stirred for 16 h, exposed to ambient air via a drying tube. 300 ml of CH_2Cl_2 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 (CCl_4).

(d) *Iodothiocyanation.* Replacement of CH_3OH with $NaSCN$ (0.100 mol) and $(C_6H_5)_4NSCN$ (0.003 mol) yielded **3d** (0.021 mol, 52%) as a colorless oil.

Preparation of cis-cyclohexane-1,2-diol (4**).** A mixture of I_2 (0.050 mol), **1** (0.040 mol), CH_3COOH (0.100 mol) and

NO^+BF_4^- (0.0008 mol) was stirred for 40 h, exposed to ambient air via a drying tube. After 16 h, a second portion of NO^+BF_4^- was added to ensure complete conversion. After work-up (column chromatography omitted), a pale brown liquid resulted, which was refluxed with CH_3COOK (0.040 mol) in 150 ml of CH_3COOH for 16 h. After addition of $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$, washing of the organic layer with H_2O , aq. $\text{Na}_2\text{S}_2\text{O}_3$, H_2O and drying, a pale brown crystalline mass was obtained after evaporation [$>95\%$ *cis*-diacetoxycyclohexane (GLC)]. The crude mass was dissolved in 200 ml of benzene and treated with 15 g of KOH in 150 ml of CH_3OH under reflux for 2 h. 20 ml of H_2O were added and the reaction product obtained after evaporation was extracted with 6×100 ml of CH_2Cl_2 , dried, evaporated and recrystallized from CCl_4 to yield **4** (0.031 mol, 78%) as colorless crystals, m.p. 96–98°C.

Preparation of bis(2-iodocyclohexyl) ether (5a). A mixture of I_2 (0.067 mol), **1** (0.120 mol), and NO^+BF_4^- (0.001 mol) in 300 ml of CH_2Cl_2 was stirred under O_2 for 7 days and additional portions of NO^+BF_4^- (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 $(\text{C}_4\text{H}_9)_3\text{SnH}$ and Na_2S . **5a** (0.0092 mol) and $(\text{C}_4\text{H}_9)_3\text{SnH}$ (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 (**5b**). When **5a** (0.016 mol) and Na_2S (0.090 mol) were refluxed in 70 ml of *n*- $\text{C}_3\text{H}_7\text{OH}$, bis(3-cyclohexenyl) ether (**5c**, 0.015 mol, 96%) was obtained as a colorless oil after addition of $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$, washing, drying, evaporation and chromatography.

Formation of 3-substituted cyclohexenes. When the iodo-functionalization reactions presented above were performed in CH_3CN , 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^+BF_4^- (0.0008 mol) were stirred under O_2 in 40 ml of CH_3COOH and 15 ml of CH_3CN in the presence, as well as in the absence, of I_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 ^1H and ^{13}C NMR spectroscopy, **6c** as a mixture of two diastereomeric forms.

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

References

1. March, J. *Advanced Organic Chemistry*, 3rd ed., Wiley, New York 1985; (a) pp. 724–725; (b) pp. 726–734.
2. Radner, F. *J. Org. Chem.* 53 (1988) 3548.
3. (a) Sumrell, G., Wyman, B. M., Howell, R. G. and Harrey, M. C. *Can. J. Chem.* 42 (1964) 2710; (b) Skell, P. S. and Pavlis, R. R. *J. Am. Chem. Soc.* 86 (1964) 2956; (c) Zanger, M. and Rabinowitz, J. L. *J. Org. Chem.* 40 (1975) 248; (d) Ayres, R. L., Michejda, C. J. and Rack, E. P. *J. Am. Chem. Soc.* 93 (1971) 1389.
4. Cambie, R. C., Chambers, D., Rutledge, P. S., Woodgate, P. D. and Woodgate, S. D. *J. Chem. Soc., Perkin Trans. 1* (1981) 33; Woodgate, P. D., Janssen, S. J., Rutledge, P. S., Woodgate, S. D. and Cambie, R. C. *Synthesis* (1984) 1017.
5. Cambie, R. C., Hayward, R. C., Roberts, J. L. and Rutledge, P. S. *J. Chem. Soc., Perkin Trans. 1* (1974) 1858; Cambie, R. C. and Rutledge, P. S. *Org. Synth.* 59 (1979) 169 and references therein.
6. Cambie, R. C., Hume, B. A., Rutledge, P. S. and Woodgate, P. D. *Aust. J. Chem.* 36 (1983) 2569.
7. Barluenga, J., Martinez-Gallo, J. M., Nájera, C. and Yus, M. *J. Chem. Soc., Chem. Commun.* (1985) 1422.
8. Motohashi, S., Satomi, M., Fujimoto, Y. and Tatsuno, T. *Chem. Pharm. Bull.* 31 (1983) 1788; Serguchev, Y. A. and Gutsulyak, R. B. *J. Org. Chem. USSR* 21 (1985) 906.
9. Ogata, Y. and Aoki, K. *J. Org. Chem.* 31 (1966) 1625.
10. Mangoni, L., Adinolfi, M., Barone, G. and Parilli, M. *Gazz. Chim. Ital.* 105 (1975) 377.
11. Horiuchi, C. A. and Satoh, J. Y. *Chem. Lett.* (1988) 1209.
12. Barluenga, J., Gonzalez, J. M., Campos, P. J. and Asensio, G. *Angew. Chem., Int. Ed. Engl.* 24 (1985) 319.
13. Barluenga, J., Rodriguez, M. A., Campos, P. J. and Asensio, G. *J. Chem. Soc., Chem. Commun.* (1987) 1491.
14. Cambie, R. C., Noall, W. I., Potler, G. J., Rutledge, P. S. and Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* (1977) 226.
15. Cornforth, J. W. and Green, D. T. *J. Chem. Soc. C* (1970) 846.
16. Forbes, C. P., Goosen, A. and Lave, H. A. H. *J. S. African Chem. Inst.* 25 (1972) 144; *J. Chem. Soc., Perkin Trans. 1* (1974) 2346.
17. Cambie, R. C., Hayward, R. C., Lindsay, B. G., Phan, A. I. T., Rutledge, P. S. and Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* (1976) 1961.
18. Olah, G. A., Salem, G., Staral, J. S. and Ho, T. L. *J. Org. Chem.* 43 (1978) 173; Olah, G. A. and Gupta, B. G. B. *J. Org. Chem.* 45 (1980) 3532.
19. Heumann, A. and Åkermark, B. *Angew. Chem., Int. Ed. Engl.* 23 (1984) 453; Uemura, S., Fukuzawa, S., Toshimitsu, A. and Okano, M. *Tetrahedron Lett.* 23 (1982) 87.

Received May 19, 1989.