Cycloadditions in Syntheses. LII. 1) Stereochemical Pathways of 1-Isoquinoline–Chloroethylene Photo[2 + 2]cycloaddition: Determination of Regio- and Stereostructures of the Products and Explanation for Their Formation

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The cycloaddition of isoquinoline and its N-methyl derivative to all the chlorinated ethylenes has been studied. The structures of all of the photoadducts were determined on the basis of X-ray crystallographic analysis as well as nuclear magnetic resonance spectroscopy and it was found that the cyclobutane rings in the adducts took puckered conformation. The details of the two-step closure process via biradical intermediates are discussed and it is concluded that α-bond rotation prior to spin relaxation in the biradical intermediates takes a primary role in determination of the stereochemical outcome. The interesting fact that more trans products are formed from cis-dichloroethylene and more cis products from trans-dichloroethylene can also be explained in terms of the present proposal.

Keywords: photocycloaddition; isoquinoline; halogenated ethylene; X-ray analysis; cyclobutane; conformation; pucker conformation; biradical intermediate

Photosensitized cycloaddition reactions to form cyclobutanes have been extensively studied as regards both mechanism and synthetic utility. The structural elucidation of a number of stereoisomers represented a massive problem, and so olefins were required for which the orientations of the substituents in the products might be elucidated by nuclear magnetic resonance (NMR) spectroscopy. For this reason the chloroethylenes have often been selected, and, in the event, the structures of all adducts were more easily resolved than with other derivatives in which the substituents showed significant coupling with the cyclobutane protons. However, use of NMR spectroscopy as the only tool for stereochemical determination of cyclobutane derivatives sometimes did not give a definite answer. Though the method is more reliable in the case of β-lactams or cyclobutanes which can only exist in a planar conformation, 2) the flexibility of the cyclobutane ring and the possible existence of several conformers 3) (planar and puckered conformations) make this method unreliable, since the relative positions in space of the various protons and groups in the cyclobutane ring may be poorly defined.

For several years, we have been studying the photo[2 + 2]-cycloadditions of a variety of heteroaromatics having an enone (e.g. 2-quinolones) or vinylogous enone function (e.g. 1-Isoquinolones) to olefins, aiming to use the reactions mainly for the construction of cyclobutane-fused heteroaromatics. 4) Though we have found that all of the reactions proceeded with high regioselectivity, the stereoselectivity of the reactions remained to be elucidated (Chart 1).

In this paper, we have examined the photoaddition of 1-Isoquinolones to chloroethylenes in order to clarify the stereochemical features and to obtain a better understanding of these photocycloaddition reactions. For convenience of exposition, this paper will be divided into three sections: 1) elucidation of the structures of the photoadducts by NMR spectroscopy, 2) verification of the stereostructures by X-ray crystallographic analysis, and 3) proposal of possible reaction mechanisms which account for all aspects (regio- and stereoselectivities) of the photoaddition of 1-Isoquinolones to a variety of chloroethylenes.

Results and Discussion

Photoaddition of 1-Isoquinolones to Chloroethylenes and Elucidation of the Structures of the Photoadducts by 1H-NMR Spectroscopy. The chloroethylenes used in this study were vinyl chloride, 1,1-dichloroethylene, trans- and cis-1,2-dichloroethylenes, trichloroethylene, and tetrachloroethylene, and all of them were found to photoadd both to 1-Isoquinolone (1): throughout this paper, all of the products derived from 1 are represented by primed numerals: 2', 3', 4'... to the 2-methyl derivative (1): all of the products derived from 1 are represented by numerals: 2, 3, 4...).

As will be described in detail in the third section, except for the trichloroethylene adducts, the major adducts are always the ones having more chlorine atoms at the 1-position than at the 2-position. Also, since none of the adducts epimerized under basic conditions (e.g. treatment with potassium carbonate or basic alumina in methanol), it is evident that they all have the thermodynamically more stable cis-configuration between C2=H and C8=H (characteristic 1).

In this section, we describe how the structures of the corresponding adducts were elucidated by 1H-NMR spectroscopy. Before carrying out structure analysis of the adducts, it is necessary to know whether the cyclobutane conformations are planar or puckered. In the latter case, two conformations (A or B) are possible. As mentioned in section 2, the structures of some of the adducts were
determined unequivocally by X-ray analysis and found to be puckered (conformation A or B) in all cases (characteristic 2). Throughout this paper, the position and stereochemistry of hydrogen and chlorine atoms on the cyclobutane ring are expressed according to the numbering shown in Fig. 1.

Based on the above two characteristics (1 and 2), the following structures were assigned for all of the adducts (2—14 and 2′—14′) by NMR spectroscopy. Since the adducts derived from 1 are soluble in CDCl₃ without exception, the detailed analysis was carried out for 2—14.

Since the adducts derived from 1,2-dichloroethenyls involved fundamental problems concerning the stereo-selectivity of the photoaddition reactions, their structure elucidation will be discussed at the outset.

As will be discussed in detail in section 3, four adducts (4—7) were obtained from photoaddition of the isoquinolone (1) to the dichloroethylenes, irrespective of the olefins used. However, the main adduct (5) derived from the cis-olefin differed from that [5′: the structure was determined

![Diagram](image_url)

**Chart 2.** Only the Numerals for the Adducts (2—14) Derived from 2-Methyl-1-isoquinolone (1: R = Me) are Shown Use of the parent isoquinolone (1′: R = H) instead of 1 gave in all cases the corresponding adducts (2′—14′).

**Table 1.** ¹H-NMR (500 MHz) Data for 2-Methyl-1-isoquinolone—1,2-Dichloroethylene Adducts (4—7)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>1'</th>
<th>2</th>
<th>2'</th>
<th>2a</th>
<th>8b</th>
<th>J (Hz)</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Vicinal</td>
<td></td>
</tr>
<tr>
<td>4B</td>
<td></td>
<td>4.56</td>
<td>4.66</td>
<td>4.46</td>
<td>4.46</td>
<td>4.14</td>
<td>1.2, 2 = 7.4, 1.8b = 3.8, 2.2a = 7.4, 2a, 8b = 10.4</td>
<td>1.2a = 1.4, 2.8b = 1.4</td>
</tr>
<tr>
<td>5A</td>
<td></td>
<td>4.26</td>
<td>4.62</td>
<td>4.70</td>
<td>3.82</td>
<td></td>
<td></td>
<td>1.2 = 6.7, 1.8b = 7.4, 2.2a = 6.7, 2a, 8b = 9.4</td>
</tr>
<tr>
<td>6B</td>
<td>4.54</td>
<td></td>
<td>4.22</td>
<td>4.10</td>
<td>4.34</td>
<td></td>
<td></td>
<td>1.2 = 7.6, 1.8b = 7.6, 2.2a = 7.6, 2a, 8b = 9.9</td>
</tr>
<tr>
<td>7B</td>
<td>5.03</td>
<td></td>
<td>4.99</td>
<td>4.54</td>
<td>4.32</td>
<td></td>
<td></td>
<td>1.2 = 8.2, 1.8b = 8.2, 2.2a = 5.9, 2a, 8b = 8.8</td>
</tr>
</tbody>
</table>
by X-ray diffraction analysis (*vide infra*) from the trans-
olefin. 1H-NMR spectral data for 4–7 are summarized in Table I.

Since the conformations of cyclobutanes found in crystals are retained in solution, the structure of 4 is automatically determined as 4B (see Fig. 3 for X-ray crystallographic analysis of 4'B).

Since \( J_{1,2a} = 0 \) in the spectrum of 6 eliminates the possibility of the puckered conformation (A), 6B is the only possible puckered structure for 6. Appreciable long-range coupling (\( J_{2,8b} = 2.9 \)Hz) in the spectrum of 7 suggests strongly that these two hydrogen atoms are in the W-
configuration and hence the structure should be 7B.

By considering the appreciable coupling constants (\( J_{1,8b} \) and \( J_{1,2} = 7–8 \)Hz), the structure of 5 can be deduced as 5A. This is because, if 5B is the structure, the corresponding constants are expected to be much smaller in the puckered cyclobutanes, the coupling constants between the trans-oriented vicinal protons (both in quasi-equatorial conformation) are the smallest (ca. 3 Hz) among all of the possible vicinal coupling constants).

Since the spectra of the adducts (4'-7') derived from the 2-unsubstituted isoquinolone (1') closely resembled those of the corresponding isomers (4–7), the structures of 4'–7' could also be assigned readily. The major adduct (5') derived from cis-1,2-dichloroethylene has the 1,2-trans configuration with puckered cyclobutane 5'A, while that derived from the trans-olefin has the 1,2-cis configuration with the puckered ring structure 4'B.

The adducts derived from 1 by photoaddition to vinyl chloride can also be assigned. Thus, the major adduct was assigned as the 1-exo chloro derivative (2A) with the A-puckered ring, since no appreciable long-range coupling was observed. In the alternative structure (2B), appreciable long-range coupling (\( J_{2,8b} \)) is expected due to the W-
configuration. The X-ray structure (Fig. 2) confirmed the above assignment (*vide infra*). The minor product was deduced on the basis of characteristic 1 to be the 1-endo chloro derivative (3B) and this assignment is in good accordance with its NMR spectrum, which clearly showed the long-range coupling (\( J_{2,8b} = 2.8 \)Hz) due to the expected W-configuration.

The similarity of the spectra shows that the photoaddition of the 2-unsubstituted derivative (1') to vinyl chloride also proceeded with the same stereoselectivity.

The structures of the adducts derived by photoaddition to 1,1-dichloroethylene were readily determined. Here, the major product derived from 1 was assigned as the 1,1-
dichloro derivative (8B), whose B-conformation is again supported by \( J_{2,8b} = 2.5 \)Hz. The minor product is obviously the regio-isomer (9) with B-conformation, since the vicinal coupling between H-1' and H-8b (trans-diastereomeric relationship) expected for 9A is not so large (3.6 Hz).

In the photoadditions mentioned above, marked regio-
selectivity giving the more highly substituted chlorine der-
avatives at the 1-position is observed. This regioselectivity, however, vanishes in the photoaddition to trichloroethylene. Thus, four isomers (10–13) were obtained in comparable

### Table II. 1H-NMR Data for 2-Methyl-1-isoquinolone-Vinyl Chloride Adducts (2–3)

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>1'</th>
<th>2</th>
<th>2'</th>
<th>2a</th>
<th>8b</th>
<th>J (Hz)</th>
<th>Other</th>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>Vicinal</td>
<td></td>
</tr>
<tr>
<td>2A</td>
<td></td>
<td>4.43</td>
<td>2.64</td>
<td>2.86</td>
<td>4.41</td>
<td>3.94</td>
<td>1.2', 2.2', 3.2'</td>
<td>2.2' = 12.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.2, 2.2, 3.2</td>
<td>2.2, 3.2 = 0</td>
</tr>
<tr>
<td>3B</td>
<td>4.65</td>
<td>3.12</td>
<td>2.43</td>
<td>4.08</td>
<td>4.29</td>
<td>1.2, 2.2, 3.2</td>
<td>2.2, 3.2 = 0</td>
<td></td>
</tr>
<tr>
<td>2A</td>
<td></td>
<td>4.52</td>
<td>2.67</td>
<td>2.75</td>
<td>4.51</td>
<td>3.89</td>
<td>1.2, 2.2, 3.2</td>
<td>2.2, 3.2 = 0</td>
</tr>
<tr>
<td>3B</td>
<td>4.66</td>
<td>3.05</td>
<td>2.48</td>
<td>4.16</td>
<td>4.26</td>
<td>1.2, 2.2, 3.2</td>
<td>2.2, 3.2 = 0</td>
<td></td>
</tr>
</tbody>
</table>

### Table III. 1H-NMR Data for 2-Methyl-1-isoquinolone-1,1-Dichloroethylene Adducts (8 and 9)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>1'</th>
<th>2</th>
<th>2'</th>
<th>2a</th>
<th>8b</th>
<th>J (Hz)</th>
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<td></td>
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<td></td>
<td></td>
<td>Vicinal</td>
<td></td>
</tr>
<tr>
<td>8B</td>
<td></td>
<td>3.39</td>
<td>3.09</td>
<td>4.32</td>
<td>4.57</td>
<td>2.2a, 6.2, 2.2a, 4.3</td>
<td>2.2' = 14.2, 2.8b = 2.5, 2.8b = 1.5</td>
<td></td>
</tr>
<tr>
<td>9B</td>
<td>2.95</td>
<td>3.47</td>
<td>4.72</td>
<td>4.04</td>
<td>1.8b, 9.5, 1.8b, 3.6</td>
<td>1.2a = 1.4, 1.2a = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8'B</td>
<td></td>
<td>3.46</td>
<td>3.10</td>
<td>4.52</td>
<td>4.59</td>
<td>2.2a, 6.5, 2.2a, 4.5</td>
<td>2.2' = 13.5, 2.8b = 2.0, 2.8b = 0</td>
<td></td>
</tr>
<tr>
<td>9'B</td>
<td>3.03</td>
<td>3.45</td>
<td>4.74</td>
<td>4.06</td>
<td>1.8b, 9.5, 1.8b, 5.5</td>
<td>1.2a = 2.0, 1.2a = 1.0</td>
<td></td>
<td></td>
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</tbody>
</table>

### Table IV. 1H-NMR Data for 2-Methyl-1-isoquinolone-Trichloroethylene Adducts (10–13)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>1'</th>
<th>2</th>
<th>2'</th>
<th>2a</th>
<th>8b</th>
<th>J (Hz)</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Vicinal</td>
<td></td>
</tr>
<tr>
<td>10B</td>
<td></td>
<td>4.62</td>
<td>4.62</td>
<td>4.82</td>
<td>4.07</td>
<td>1.8b, 5.4, 2.8b, 10.6</td>
<td>1.2a = 1.2</td>
<td></td>
</tr>
<tr>
<td>11B</td>
<td></td>
<td>4.60</td>
<td>4.60</td>
<td>4.33</td>
<td>4.63</td>
<td>2.2a, 7.3, 2.8b, 9.7</td>
<td>2.8b = 1.3</td>
<td></td>
</tr>
<tr>
<td>12B</td>
<td></td>
<td>5.13</td>
<td>5.13</td>
<td>4.79</td>
<td>4.57</td>
<td>2.2a, 6.0, 2.8b, 9.0</td>
<td>2.8b = 2.5</td>
<td></td>
</tr>
<tr>
<td>13B</td>
<td>5.14</td>
<td>—</td>
<td></td>
<td>4.72</td>
<td>4.34</td>
<td>1.8b, 9.8, 2.8b, 9.9</td>
<td>1.2a = 0</td>
<td></td>
</tr>
</tbody>
</table>

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yields. The structures of all adducts were tentatively assigned as having B-conformation.

The structure of 10B was confirmed by X-ray crystallographic analysis (Fig. 4). The structure 12B was supported by $J_{2,2b}=2.5$ Hz, which is consistent only with the B-conformation. The lack of $J_{1,2a}$ eliminates the A-conformation for 13 and hence, its structure is assigned as 13B. Finally, since two vicinal coupling constants ($J_{2,2a}$ and $J_{2a,2b}$) are of the order of 7–10 Hz, the structure (11A) can be ruled out [the coupling constant between quasi-equatorial hydrogens (trans to each other) would be small (ca. 3 Hz, vide supra)].²⁶

Regarding the conformations of the cyclobutane ring in the cyclobutisoquinolones (2–13 and 2′–13′), the following can be said. 1) All of them exist in puckered conformation, though the angle is much smaller than 30–35° in usual cyclobutanes. In the latter case, the long-range coupling constants due to the W-configuration are 5–6 Hz. 2) The fact that only two cases (2A or 2′A and 5A or 5′A) exist in A conformation clearly shows that preference of conformer B over conformer A is a general phenomenon in this series of compounds. The exceptional preference for the A conformations for 2 and 5 series is probably due to all chlorine atoms taking quasi-equatorial conformation in these two species. 3) The absence of the conformers having a 1,3-cis relationship between chlorine and nitrogen atoms (both quasi-axial relative to the puckered cyclobutane ring) probably reflects an unfavorable electronic (and/or steric) interaction.

While no information is available for 14 or 14′ from the NMR spectra, the remarks mentioned above (1–3) suggest that the structures of 14 and 14′ probably both take the B-conformation.

X-Ray Crystallographic Analyses of 2A, 4′B, and 10B

In order to confirm definitively the structures of these photocycloadducts and to gain further insight into their conformations, three adducts were subjected to X-ray crystallographic analyses.

As is clear from these data (Figs. 2–4), the cyclobutane rings in them are all puckered in one of two ways: A [puckered with C-2 and C-8b carbons on the same side (upper side)] and B [puckered with C-1 and C-2a carbons on the same side (upper side)]. By detailed analysis of the X-ray data (see Experimental), the angles [defined as $180°-\theta$ (the dihedral angle between the two planes: C-1, C-2, C-2a and C-1, C-2a, C-8b)] are 23.97° for 2A, 30.36 for 4′B, and 17.58° for 10B, respectively.

As mentioned in the foregoing section, we may reasonably assume that these adducts have the same puckered conformations in solution.

A Proposal for the Reaction Mechanism Accounting for All Aspects (Regio- and Stereoselection) of the Photoaddition of 1-Isouquinolones to Chloroethylenes

Since the structure determinations of all of the photoadducts derived from the isoquinolones (1 and 1′) and chloroethylenes have been accomplished, it is now possible to discuss the mechanism of the photoaddition.

Table V summarizes the yields of the adducts derived from the photoaddition.
It has already become clear that, in the photoaddition to mono-substituted olefins, 1 and its N- and/or C-substituted derivatives afford 1-substituted cyclobutidine as the major products.\(^7\)\(^-\)\(^9\) The same regioselectivity was observed in the present study. Thus, when 1 was photoadduced to vinyl chloride or 1,1-dichloroethylene, the photoadducts (2, 3, and 8) more highly substituted at the 1-position were obtained and the amount of the regio-isomers (9) formed was low, if any. Hence, it could be assumed that the present reactions proceed through the biradical intermediate formed from excited isoquinolone (T\(1\)) and chloroethylenes (S\(0\)). Since tetrachloroethylene also afforded the cycloaduct (14) in a comparable rate to the photoadditions to the less highly substituted ethylenes, it seems clear that reversion from the intermediate is not significant in the present study.\(^10\)

In the case of photoaddition to 1,1-dichloroethylene, the reaction pathway shown in Chart 3 can thus be proposed. Among all of the four possible intermediates (A—D) shown in Chart 3, A and B are considered as the actual intermediates. The adduct (8) corresponding to the more thermodynamically stable biradical (A) is formed predominantly over the adduct (9) corresponding to the less stable one (C).

Since the main interest of the present study is how to account for the stereoselectivity in these photoadditions, we will consider the photoaddition of 1 to 1,2-dichloroethylene first (cf. Table V). According to the proposed pathway (Chart 3), the first bond formation occurs at the 3-position of the isoquinolone. Therefore, the relative configuration of the 2- and 2a-positions in the adducts must be determined in the biradical formations step.

For the addition of the trans-ethylene, preferential formation of biradical (F) over (H) is expected and this indicates that approach of two components [1 in the triplet state (T\(1\)) and the olefin in the singlet state (S\(0\))] as in E is preferred to G. After the intermediates (F and H) are formed, there are two possible pathways (a and b) from each biradical to the final adducts (4—7). Taking F as an example, these are path a which corresponds to spin inversion with retention of configuration at all of the reacting centers to give 6 and path b which corresponds the terminal C—C bond rotation prior to the spin inversion. Since 4 was the major product, path b is the preferred one\(^11\) (ratio of 4/6 = ca. 3). Assuming that approach of the cis-ethylene to 1 as in I is preferable to K, the preference of path b from the biradical (J) thus formed would also account for the predominant formation of 5 (ratio of 5/7 = ca. 2). The preference of E and I over G and K reveals that endo-approach (throughout this paper,

<p>| Table V. Photoaddition of 1-Isouquinolones (I and I') to a Variety of Chloroethylenes in Methanol |
|------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Chloroethylene</th>
<th>Product (Yields in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>ClCH = CH₂</td>
<td>2A (67), 3B (10)</td>
</tr>
<tr>
<td>2</td>
<td>I'</td>
<td>The same olefin</td>
<td>2A (50), 3B (14)</td>
</tr>
<tr>
<td>3</td>
<td>I</td>
<td>cis-ClCH = CHCl</td>
<td>4B (7), 5A (44)</td>
</tr>
<tr>
<td>4</td>
<td>I'</td>
<td>The same olefin</td>
<td>4B (6), 5A (59)</td>
</tr>
<tr>
<td>5</td>
<td>I</td>
<td>trans-ClCH = CHCl</td>
<td>4B (32), 5A (22)</td>
</tr>
<tr>
<td>6</td>
<td>I'</td>
<td>The same olefin</td>
<td>4B (39), 5A (20)</td>
</tr>
<tr>
<td>7</td>
<td>I</td>
<td>CH₂ = CCl₂</td>
<td>8B (74), 9B (9)</td>
</tr>
<tr>
<td>8</td>
<td>I'</td>
<td>The same olefin</td>
<td>8B (72), 9B (11)</td>
</tr>
<tr>
<td>9</td>
<td>I</td>
<td>ClCH = CCl₂</td>
<td>10B (32), 11B (19)</td>
</tr>
<tr>
<td>10</td>
<td>I'</td>
<td>The same olefin</td>
<td>10B (31), 11B (18)</td>
</tr>
</tbody>
</table>

Chart 3

Chart 4

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we define the *endo*- and *exo*-approaches of chloroolefins relative to the C-4 position of the isoquinolines (1 and 1') as preferable to the corresponding *exo*-approach. We term this, hereafter, as the primary *endo* rule.

It should be noted that the sigma bond rotation of the biradicals (F, J, etc.) to give the final four-membered ring compounds (4–7) obeys the least-motion principle. Thus, as depicted in Chart 4, the outer terminal p-lobe (unshaded one) rotates inward (b) and overlaps with the inner p-lobe (shaded one) of the pro-C of the to give the final products. The *endo*-preference (formation of M) as well as the least-motion principle mentioned above (sigma-bond rotation depicted by dotted line in M) also account for the predominant formation of 2 over 3 (ratio 2:3 = 7) by the photoaddition of vinyl chloride to the isoquinolines (1 and 1').

The photoaddition of trichloroethylene to 1 gave 10–13 in the amounts of 10 ≈ 12 ≈ 11 > 13. Two problems arise in trying to explain the results.

The first one is, in this reaction, the amount of the more 1-substituted adducts (11 and 12) are comparable with those of the other regioisomers (10 and 13). Probably, this may be explained by assuming that the stabilities of −CHCl and −Cl radicals do not differ significantly as compared with those of −CHCl and −CH radicals. The second problem is how to explain the yields of the four adducts. This can be done if one assumes that secondary *endo*-preference holds. The secondary *endo* rule implies that, though the afore-mentioned primary *endo* rule (chlorine atom relative to C of the isoquinoline ring) takes the primary role, if this is satisfied, this secondary preference (chlorine atom of the olefins relative to the 3-position of 1) determines the preferred approaches of the two components (chloroolefins and isoquinolines) so that this secondary effect is satisfied. Since U (the precursor of 13) does not satisfy the primary *endo* rule, the observation that the amount of 13 in the above reaction is least explained. Since the precursor (R) satisfies the primary *endo* rule and (S) satisfies the secondary one, the yields of 12 and 10 are larger than that of 11, whose precursor (T) does not satisfy the secondary rule.

**Conclusions**

In the present study dealing with photo[2+2]cycloaddition of 1-isoquinolones to chloroolefins, we have determined the structures of the photoproducts (both their relative configurations and conformations) and proposed a mechanism accounting for their formations. Dilling et al. as well as Loutfy and de Mayo have previously examined the photoaddition of cyclopentene to 1,2-dichloroethylenes and found that the configuration of the adducts formed is the opposite to that of the starting olefins. That is, more *trans* products are formed from *cis*-dichloroethylene and more *cis* products from the *trans* ethylene, the same trend which was observed in our study. The same phenomenon was also observed recently by Sano et al. in the photoaddition of some dioxyxpyrroles to a variety of olefins. Bartlett and coworkers have discussed the cause of different product distributions from the cycloaddition of cyclopentadiene to a variety of olefins, showing the same trend as above, so our mechanism seems to be also applicable to related photoaddition reactions, in general. We are now hoping to extend this approach to the photoaddition of quinolines to olefins, and also to develop chemical manipulations of the photoproducts obtained in this study in order to utilize this reaction as a means to introduce a functionalized side chain at the 4-position of the isoquinoline ring.

**Experimental**

All melting points were determined on a micro-hot stage (Yanagimoto) and are uncorrected. Infrared (IR) spectra were recorded on a JEOL IR spectrometer, ultraviolet (UV) spectra with a Hitachi 320 spectrometer, and 1H-NMR spectra on a JEOL JNM-FX 500 spectrometer, with tetramethylsilane as an internal standard. Mass spectra (MS) were taken with a JEOL JMS-D102 spectrometer or a JEOL DX-303 spectrometer. Silica gel used for column chromatography was Wako gel C-200, and the ratios of solvent mixtures for chromatography are shown as volume/volume.

Photocyclizations on a relatively large scale (500 mg–2 g of isoquinolines) were carried out under argon in a Pyrex immersion apparatus equipped with a Riko 450 W high-pressure mercury lamp cooled both internally with running water and externally by ice-water, and correspond to irradiation at >300 nm. Photocyclizations on a relatively small scale (100–200 mg) were carried out using a Rayonet photochemical reactor (RPR-3000A) and correspond to irradiation at 300 nm.

Photocyclization of 1,2-difluoro-1' and 1' with Vinyl Chloride A solution of 1' (1.74 g, 12 mmol) and vinyl chloride (41 ml, 0.6 mol) in MeOH (1 l) was irradiated at >300 nm for 3 h. The residue obtained by evaporation of the solvent was subjected to column chromatography (silica gel, 120 g). Elution with hexane–AcOEt (1:3) gave 1,383 mg (56%) of (15*.2a*.8b*.5*s)-1-chloro-4-oxo-1,2,2,3,4,5-hexahydrocyclobut[c]isoquinoline (2A). Further elution with hexane–AcOEt (1:1) gave 342 mg (14%) of (15*.2a*.8b*.5*s)-1-chloro-4-oxo-1,2,2,3,4,5-hexahydrocyclobut[c]isoquinoline (3B).

2'A: mp 173–175°C, colorless needles (acetone–hexane). IR (CHCl3): 3050, 1665 cm⁻¹. 1H-NMR (CDCl3, 300 MHz) δ: 2.67 (1H, ddd, J = 12.2, 7.2, 7.2 Hz, 2-Hαβ), 2.75 (1H, ddd, J = 12.2, 8.1, 3.4 Hz, 2-Hαβ), 3.80 (1H, ddd, J = 8.1, 7.2 Hz, 8-Hβ), 4.51 (1H, m, 2a-H), 4.52 (1H, ddd, J = 8.1, 7.2, 7.2 Hz, 1-H), 6.30 (1H, brs, −NCl), 7.24 (1H, dd, J = 7.8, 1.0 Hz, 5-Hβ), 7.45 (1H, dt, J = 1.0, 7.8 Hz), 7.56 (1H, dt, J = 1.0, 7.8 Hz), 8.19 (1H, ddd, J = 7.8, 1.0 Hz, 4-Hα). Anal. Caled for C13H11Cl2NO: C, 63.62; H, 4.85; Cl, 17.07; N, 6.75. Found: C, 63.37; H, 4.92; Cl, 17.09; N, 6.65.

3'B: mp 182–184°C, colorless needles (acetone–hexane). IR (CHCl3): 3046, 1663 cm⁻¹. 1H-NMR (CDCl3, 300 MHz) δ: 2.48 (1H, ddd, J =
Photoreaction of 2-Methylisouquinolin-1(2H)-one (1) with cis-1,2-Dichloroethylene

A solution of 1 (145 mg, 1 mmol) and cis-1,2-dichloroethylene (1.94 g, 20 mmol) in MeOH (100 ml) was irradiated at 300 nm for 3 h. Work-up and column chromatographic separation (silica gel, 55 g) of the products as described above gave 15 mg (6%) of 4B, 15 mg (63%) of a mixture of 5A and 6B, and 13 mg (6%) of 6A.

Photoreaction of 2-Methylisouquinolin-1(2H)-one (1) with trans-1,2-Dichloroethylene

A solution of 1 (477 mg, 3 mmol) and trans-1,2-dichloroethylene (8.73 g, 90 mmol) in MeOH (230 ml) was irradiated at 300 nm for 2 h. After removal of the solvent, the residue was chromatographed over silica gel (46 g). Elution with hexane–acetonitrile (5:1) gave 246 mg (46%) of 7B (trans-1,2-dichloroethylene) [2,3,4,8b-hexahydroxydibenz[b]cyclo[6]quinolone (4B) and 295 mg (39%) of a mixture of (1R,2R,2aR,8bS)-1,2-dichloro-3-methyl-4-oxo-1,2,3,4,8b-hexahydrodibenz[b]cyclo[6]quinolone (5A) and (1S,2S,2aR,8bS)-1,2-dichloro-3-methyl-4-oxo-1,2,3,4,8b-hexahydrodibenz[b]cyclo[6]quinolone (6B) in a ratio of 3:1. Elution with hexane–acetonitrile (1:1) gave 122 mg (16%) of (1S,2R,2aR,8bS)-1,2-dichloro-3-methyl-4-oxo-1,2,3,4,8b-hexahydrodibenz[b]cyclo[6]quinolone (7B).

4B: mp 182–183°C, colorless leaves (acetone–hexane). IR (CHCl₃): 1665 cm⁻¹. ¹H-NMR (CDCl₃, 500 MHz) δ: 3.22 (2H, s, NCH₂), 4.14 (1H, dd, δ = 10.4, 3.8, 14.8 Hz, 8b-H), 4.46 (1H, dd, δ = 10.4, 7.4, 14.8 Hz, 4a-H), 4.56 (1H, dd, δ = 7.4, 3.8, 14.8 Hz, 1-H), 4.66 (1H, dd, δ = 7.4, 1.7, 14.8 Hz, 1-H), 7.13 (1H, dd, δ = 7.4, 1.7, 8.0 Hz, 1-H), 7.32 (1H, dd, δ = 7.4, 1.7, 8.0 Hz, 1-H), 8.22 (1H, dd, δ = 7.1, 1.7, 8.0 Hz, 1-H). Anal. Calc. for C₁₇H₁₁Cl₂N₂O₂: C, 56.27; H, 4.33; Cl, 27.68; N, 5.47. Found: C, 56.12; H, 4.34; Cl, 27.50; N, 5.46. The structures and ratio (1:3:1) of 5A,6B were determined by the following NMR spectral data (δ) in CDCl₃ (500 MHz): 5A: 3.19 (3H, s, NCH₃), 3.82 (2H, dd, δ = 9.4, 7.4 Hz, 8b-H), 4.26 (1H, dd, δ = 7.6, 6.7, 1.4 Hz, 1-H), 4.66 (1H, dd, δ = 7.6, 6.7, 1.4 Hz, 1-H), 7.13 (1H, dd, δ = 7.6, 1.4, 8.0 Hz, 1-H), 7.42 (1H, dd, δ = 7.6, 1.4, 8.0 Hz, 1-H), 7.52 (1H, dt, δ = 1.0, 7.8 Hz, 8.22 (1H, dd, δ = 7.1, 1.7, 8.0 Hz, 1-H), 7.21 (1H, dd, δ = 7.1, 1.7, 8.0 Hz, 1-H). 6B: mp 7.47 (1H, dt, δ = 1.0, 7.8 Hz, 8.22 (1H, dd, δ = 7.1, 1.7, 8.0 Hz).

6A: 3.42 (3H, s, NCH₃), 4.10 (2H, dd, δ = 9.9, 7.6 Hz, 2a-H), 4.22 (2H, dd, δ = 7.6, 6.8, 0.2 Hz, 4a-H), 4.34 (2H, dd, δ = 9.9, 7.6 Hz, 2a-H), 4.54 (1H, dd, δ = 7.6, 6.8, 0.2 Hz, 4a-H), 7.21 (1H, dd, δ = 7.6, 1.0, 8.0 Hz, 1-H), 7.45 (1H, dd, δ = 7.6, 1.0, 8.0 Hz, 1-H), 7.49 (1H, dt, δ = 1.0, 7.8 Hz, 8.22 (1H, dd, δ = 7.1, 1.7, 8.0 Hz). 5A: mp 162–163°C, colorless needles (acetone–hexane). IR (CHCl₃): 1662 cm⁻¹. ¹H-NMR (CDCl₃, 500 MHz) δ: 3.11 (3H, s, NCH₃), 4.32 (1H, dd, δ = 8.8, 8.2, 2.9 Hz, 8b-H), 4.54 (1H, dd, δ = 8.8, 8.2, 2.9 Hz, 8b-H), 4.99 (1H, dd, δ = 8.8, 8.2, 2.9 Hz, 4a-H), 5.03 (1H, dd, δ = 8.8, 8.2, 2.9 Hz, 1-H), 7.13 (1H, dd, δ = 7.6, 1.0, 8.0 Hz, 1-H), 7.42 (1H, dd, δ = 7.6, 1.0, 8.0 Hz, 1-H), 7.48 (1H, dt, δ = 1.0, 7.8 Hz, 8.22 (1H, dd, δ = 7.1, 1.7, 8.0 Hz). 7B: mp 171–173°C (lit. 168–169°C). ¹H-NMR (CDCl₃, 500 MHz) δ: 3.03 (3H, dd, δ = 13.5, 5.5, 1.0 Hz, 2a-H), 4.34 (1H, dd, δ = 13.5, 5.5, 1.0 Hz, 2a-H), 7.42 (1H, dd, δ = 7.2, 1.7, 2.1 Hz, 1-H), 7.51 (1H, dd, δ = 7.2, 1.7, 2.1 Hz, 1-H), 7.96 (1H, brs, δ = 1.7, 2.1 Hz, 1-H).
Photoreaction of 2-Methylisooquinolin-1(2H)-one (1) with 1,1-Dichloroethene
A solution of 1 (159 mg, 1 mmol) and 1,1-dichloroethene (2.88 g, 30 mmol) in MeOH (100 ml) was irradiated at 300 nm for 5.5 h. Work-up as described above gave 189 mg (74% of (2\(\text{a}^\ast\),8\(\text{b}\)\(\text{b}\)*)-1,1-dichloroethenyl-3-methoxy-1,4-oxa-2,1,2-dichloro-3,4,8,8a-hexahydrochalcone (9C) and 23 mg (9%) of (2\(\text{a}^\ast\),8\(\text{b}\)\(\text{b}\)*)-2,2-dichloro-3-methyl-1,4-oxa-2,1,2-dichloro-3,4,8,8a-hexahydrochalcone (9B).}

10B: mp 110—111 C, colorless needles (hexane). IR (CHCl\(_3\)): 1671 cm\(^{-1}\). \(\text{H-NMR (CDCl}_3, 500 \text{MHz})\): 3.27 (3H, s, \(-\text{NCH}_3\)), 4.07 (1H, d, \(J=10.6, 5.4 \text{Hz, 8b-H}\)), 4.72 (1H, d, \(J=9.8, 1.0 \text{Hz, 8a-H}\)), 5.92 (1H, d, \(J=10.6, 1.2 \text{Hz, 2a-H}\)), 7.22 (1H, d, \(J=7.8, 1.0 \text{Hz, 8a-H}\)), 7.43 (1H, d, \(J=1.0, 7.8 \text{Hz, 8b-H}\)), 7.53 (1H, d, \(J=7.8, 1.0 \text{Hz, 8a-H}\)). Anal. Calcd for C\(_{11}\)H\(_9\)Cl\(_2\)N\(_2\): C, 56.0; H, 3.47; Cl, 36.60; N, 4.49. Found: C, 56.4; H, 3.52; Cl, 36.40; N, 4.49.

11B: mp 171—172 C, colorless laminae (hexane). IR (CHCl\(_3\)): 1670 cm\(^{-1}\). \(\text{H-NMR (CDCl}_3, 500 \text{MHz})\): 3.45 (3H, s, \(-\text{NCH}_3\)), 4.33 (1H, d, \(J=9.7, 7.3 \text{Hz, 2a-H}\)), 4.60 (1H, d, \(J=7.8, 1.3 \text{Hz, 2b-H}\)), 4.63 (1H, d, \(J=9.8, 0.0 \text{Hz, 8a-H}\)), 5.13 (1H, d, \(J=6.0, 2.5 \text{Hz, 2b-H}\)), 7.22 (1H, d, \(J=7.8, 1.0 \text{Hz, 8b-H}\)). Anal. Calcd for C\(_{11}\)H\(_9\)Cl\(_2\)N\(_2\): C, 56.0; H, 3.47; Cl, 36.60; N, 4.49. Found: C, 56.3; H, 3.49; Cl, 36.5; N, 4.55.

13B: mp 176—178 C, colorless leaves (hexane). IR (CHCl\(_3\)): 1669 cm\(^{-1}\). \(\text{H-NMR (CDCl}_3, 500 \text{MHz})\): 3.29 (3H, s, \(-\text{NCH}_3\)), 4.34 (1H, d, \(J=9.9, 9.8 \text{Hz, 8b-H}\)), 4.72 (1H, d, \(J=9.9, 9.8 \text{Hz, 2a-H}\)), 5.14 (1H, d, \(J=9.8, 1.0 \text{Hz, 1-H}\)), 7.13 (1H, d, \(J=7.8, 1.0 \text{Hz, 5-H}\)), 7.42 (1H, d, \(J=1.0, 7.8 \text{Hz, 7.5-H}\)), 7.51 (1H, d, \(J=1.0, 7.8 \text{Hz, 7.5-H}\)), 8.24 (1H, d, \(J=7.8, 1.0 \text{Hz, 5-H}\)). Anal. Calcd for C\(_{11}\)H\(_9\)Cl\(_2\)N\(_2\): C, 56.0; H, 3.47; Cl, 36.60; N, 4.49. Found: C, 56.3; H, 3.49; Cl, 36.5; N, 4.48.

Photoreaction of 2-Methylisooquinolin-1(2H)-one (1) with Tetrachloroethylene
A solution of 1 (87 mg, 0.6 mmol) and tetrachloroethylene (9.55 g, 60 mmol) in MeOH (200 ml) was irradiated for 3.25 h. The residue was purified by recrystallization from acetone (to give 111 mg (60%) of (2\(\text{a}^\ast\),8\(\text{b}\)\(\text{b}\)*)-4-oxo-1,1,2,2-tetrachloro-1,2,3,4,8,8a-hexahydrochalcone (14B).}

14B: mp 228—229 C, colorless needles (acetone–hexane). IR (Nujol): 1675 cm\(^{-1}\). \(\text{H-NMR (DMSO-d}_6\)\): 4.93—5.07 (2H, m, 2a-H, 8b-H), 7.30—7.60 (3H, m, aromatic H), 7.98—8.18 (1H, m, 5-H), 8.73—9.02 (1H, brs, –NH). Anal. Calcd for C\(_{12}\)H\(_9\)Cl\(_2\)N\(_2\): C, 52.6; H, 2.72; Cl, 45.4; N, 4.50. Found: C, 52.3; H, 2.18; Cl, 45.88; N, 4.61.

Photoreaction of 2-Methylisooquinolin-1(2H)-one (1) with Tetrachloroethylene
A solution of 1 (318 mg, 2 mmol) and tetrachloroethylene (9.8 g, 60 mmol) in MeOH (200 ml) was irradiated for 1.5 h. Column chromatography of the residue over silica gel (19 g) gave 480 mg (74%) of (2\(\text{a}^\ast\),8\(\text{b}\)\(\text{b}\)*)-3-methyl-4-oxo-1,1,2,2-tetrachloro-1,2,3,4,8,8a-hexahydrochalcone (14B) from the eluates with hexane–AcOEt (1:3).
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14B: mp 148—149°C, colorless prisms (ether). IR (CHCl₃): 1660 cm⁻¹, 1H-NMR (CDCl₃) δ 3.23 (3H, s, -NCH₃), 4.65 (1H, d, J=10 Hz, 8-H), 4.95 (1H, d, J=10 Hz, 2a-H), 7.21 (3H, m, aromatics H), 7.99 (1H, m, 5-H). Anal. Calc'd for C₁₉H₁₄Cl₂NO: C, 44.35; H, 2.79; Cl, 43.63; N, 4.31. Found: C, 44.40; H, 2.90; Cl, 43.67; N, 4.35.

X-Ray Crystal Analyses 17 Reflecton data were collected on a Rigaku AFC-5R four-circle diffractometer controlled by the MSC/AFC program package, using Mo Kα radiation monochromated by a graphite monochromator, in the 2θ-ω scan mode. Reflecton with intensity above the 3σ (I) level were used for the structure determination. The structure was solved by the direct method using MITHRIL 18 and refined by the full-matrix least-squares method with the assumption of positional anisotropic thermal parameters for all atoms. Crystal data for 2A, 4B, and 10B are given in Table VI.

References and Notes
10) It should be noted that, when irradiated at 254 nm in an appropriate transparent solvent (this experiment was performed in a UV cell), these adducts were found to cyclodepolar to the original components with partial decomposition. Similar irradiation at ≥300 nm (irradiation source: high-pressure mercury lamp with a Pyrex filter), however, did not cause these cyclodepolymerizations to occur to any significant extent.
16) The photoaddition of 2-methy1siquinolin-1(2H)-one (1) to 1,1-dichlorooctethy1ene was performed for the first time by Dr. Toshikiko Naito (Present address: Tsukuba Research Laboratory, Etsai Co., Ltd., Tokodai 5-cho-me, Toyosato-machi, Tsukuba-gun, Ibaraki 300-16, Japan). He also found that treatment of the major adduct (88) with NaOH/MEOH gave 4-(1-chlorovinyl)-2-methy1siquinolin-1(2H)-one in an almost quantitative yield. T. Naito, Dissertation, Pharmaceutical Institute, Tohoku University (1986).
17) Final tables of the individual bond length and angles, and hydrogen and non-hydrogen atomic positions are available on request.