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

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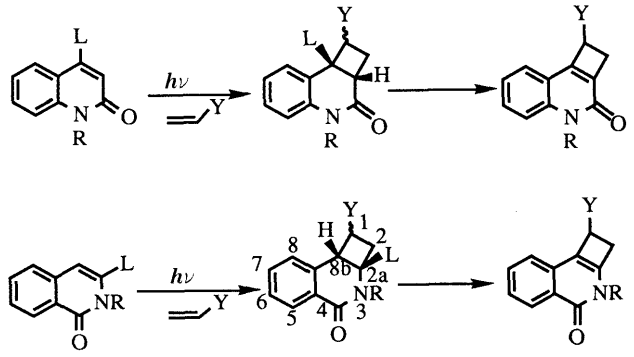
The cycloaddition of isoquinolone and its N-methyl derivative to all the chlorinated ethylenes has been studied. The structures of all of the photoadducts were determined on the basis of X-ray crystallographic analysis as well as nuclear magnetic resonance spectroscopy and it was found that the cyclobutane 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 σ-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; isoquinolone; halogenated ethylene; X-ray analysis; cyclobutane; conformation; puckered 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 cyclobutenes 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 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 regioselection, the stereoselectivity of the reactions remained to be elucidated (Chart 1).



L = a leaving group

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 ^{1}H-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′**$\cdots$) and to the 2-methyl derivative (**1**: all of the products derived from **1** are represented by numerals: **2**, **3**, **4**$\cdots$).

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 C_{2a}-H and C_{8b}-H (characteristic 1).

In this section, we describe how the structures of the corresponding adducts were elucidated by ^{1}H-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.

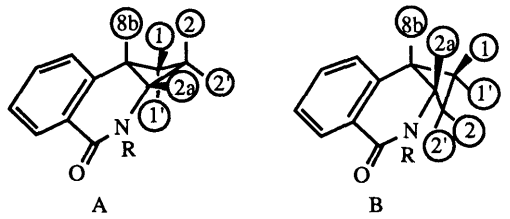


Fig. 1. Two Possible Puckered Conformation (A and B) of 4-Oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinolines

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 $CDCl_3$ without exception, the detailed analysis was carried out for **2**—**14**.

Since the adducts derived from 1,2-dichloroethylenes involved fundamental problems concerning the stereoselectivity 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 [**4′**: the structure was determined

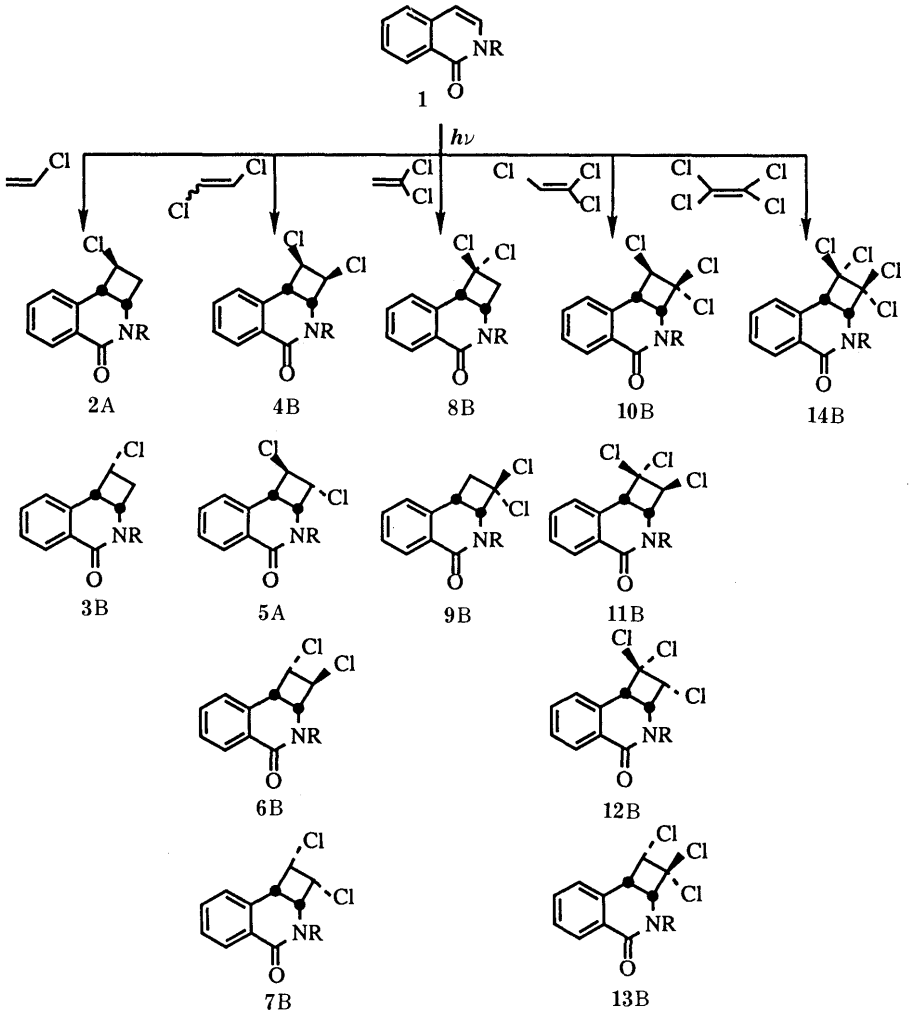


Chart 2. Only the Numerals for the Adducts (**2**—**14**) Derived from 2-Methyl-1-isoquinolone (**1**: R=Me) are Shown

Use of the parent isoquinolone (**1′**: R=H) instead of **1** gave in all cases the corresponding adducts (**2′**—**14′**).

TABLE I. ^{1}H-NMR (500 MHz) Data for 2-Methyl-1-isoquinolone–1,2-Dichloroethylene Adducts (**4**—**7**)

	δ						*J* (Hz)	
	1	1′	2	2′	2a	8b	Vicinal	Other
4B	—	4.56	—	4.66	4.46	4.14	1′,2′=7.4, 1′,8b=3.8, 2′,2a=7.4, 2a,8b=10.4	1′,2a=1.4, 2′,8b=1.4
5A	—	4.26	4.62	—	4.70	3.82	1′,2=6.7, 1′,8b=7.4, 2,2a=6.7, 2a,8b=9.4	1′,2a=1.4, 2,8b=1.6
6B	4.54	—	—	4.22	4.10	4.34	1,2′=7.6, 1,8b=7.6, 2′,2a=7.6, 2a,8b=9.9	2′,8b=0.8, 1,2a=0
7B	5.03	—	4.99	—	4.54	4.32	1,2=8.2, 1,8b=8.2, 2,2a=5.9, 2a,8b=8.8	1,2a=1.6, 2,8b=2.9

by X-ray diffraction analysis (*vide infra*)] from the *trans*-olefin. ^{1}H-NMR spectral data for **4**—**7** are summarized in Table I.

Since the conformations of cyclobutanes found in crystals[3] are retained in solution,[5] 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[6] 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].[5,6]

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-quasi*-diaxial relationship) expected for **9A** is not so large (3.6 Hz).

In the photoadditions mentioned above, marked regioselectivity giving the more highly substituted chlorine derivatives 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. ^{1}H-NMR Data for 2-Methyl-1-isoquinolone–Vinyl Chloride Adducts (**2**—**3**)

Compound	δ						J (Hz)	
	1	1'	2	2'	2a	8b	Vicinal	Other
2A	—	4.43	2.64	2.86	4.41	3.94	1',2'=7.2, 1',2'=8.0, 1',8b=8.2, 2,2a=7.2, 2',2a=3.2, 2a,8b=8.2	2,2'=12.3, (2,8b=0)
3B	4.65	—	3.12	2.43	4.08	4.29	1,2=8.1, 1,2'=8.1, 1,8b=8.1, 2,2a=8.1, 2',2a=8.1, 2a,8b=8.1	2,2'=11.8, 2,8b=2.8, (1,2a=0)
2'A	—	4.52	2.67	2.75	4.51	3.89	1',2=7.2, 1',2'=7.2, 1',8b=8.1, 2,2a=7.2, 2',2a=3.4, 2a,8b=8.1	2,2'=12.2, (2,8b=0)
3'B	4.66	—	3.05	2.48	4.16	4.26	1,2=8.3, 1,2'=8.3, 1,8b=8.3, 2,2a=8.3, 2',2a=8.3, 2a,8b=8.3	2,2'=12.1, 2,8b=3.5, (1,2a=0)

TABLE III. ^{1}H-NMR Data for 2-Methyl-1-isoquinolone–1,1-Dichloroethylene Adducts (**8** and **9**)

	δ						J (Hz)	
	1	1'	2	2'	2a	8b	Vicinal	Other
8B	—	—	3.39	3.09	4.32	4.57	2,2a=6.7, 2',2a=4.3, 2a,8b=8.9	2,2'=14.2, 2,8b=2.5, 2',8b=1.5
9B	2.95	3.47	—	—	4.72	4.04	1,8b=9.5, 1',8b=3.6, 2a,8b=10.2	1,2a=1.4, 1',2a=0
8'B	—	—	3.46	3.10	4.52	4.59	2,2a=6.5, 2',2a=4.5, 2a,8b=9.0	2,2'=13.5, 2,8b=2.0, 2',8b=0
9'B	3.03	3.45	—	—	4.74	4.06	1,8b=9.5, 1',8b=5.5, 2a,8b=9.5	1,2a=2.0, 1',2a=1.0

TABLE IV. ^{1}H-NMR Data for 2-Methyl-1-isoquinolone–Trichloroethylene Adducts (**10**—**13**)

	δ						J (Hz)	
	1	1'	2	2'	2a	8b	Vicinal	Other
10B	—	4.62	—	—	4.82	4.07	1',8b=5.4, 2a,8b=10.6	1',2a=1.2
11B	—	—	—	4.60	4.33	4.63	2',2a=7.3, 2a,8b=9.7	2',8b=1.3
12B	—	—	5.13	—	4.79	4.57	2,2a=6.0, 2a,8b=9.0	2,8b=2.5
13B	5.14	—	—	—	4.72	4.34	1,8b=9.8, 2a,8b=9.9	1,2a=0

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 $J_{2,8b}=2.5$ 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 $J_{2a,8b}$) are of the order of 7—10 Hz, the structure (**11**A) can be ruled out [the coupling constant between *quasi*-equatorial hydrogens (*trans* to each other) would be small (*ca.* 3 Hz, *vide supra*)].[5,6]

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 (**2**A or **2'**A and **5**A 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 quckered 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 **2**A, 30.36 for **4'**B, and 17.58° for **10**B, 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-Isoquinolones 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.

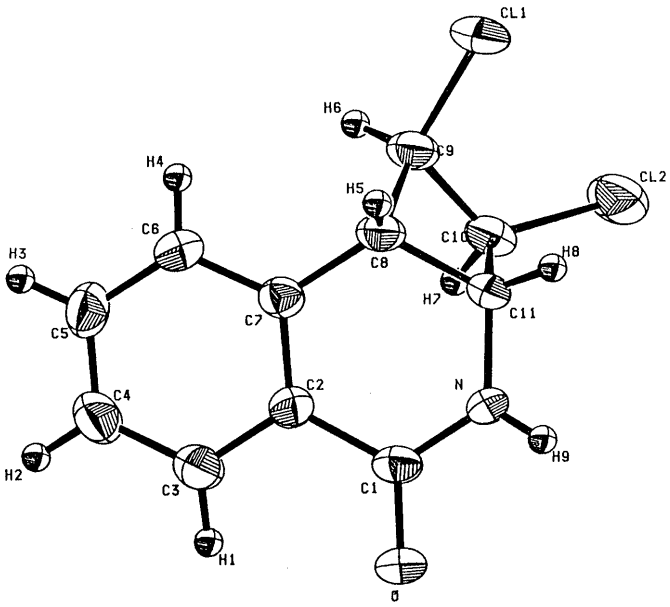


Fig. 3. ORTEP Drawing of the Molecular Structure of **4'B**

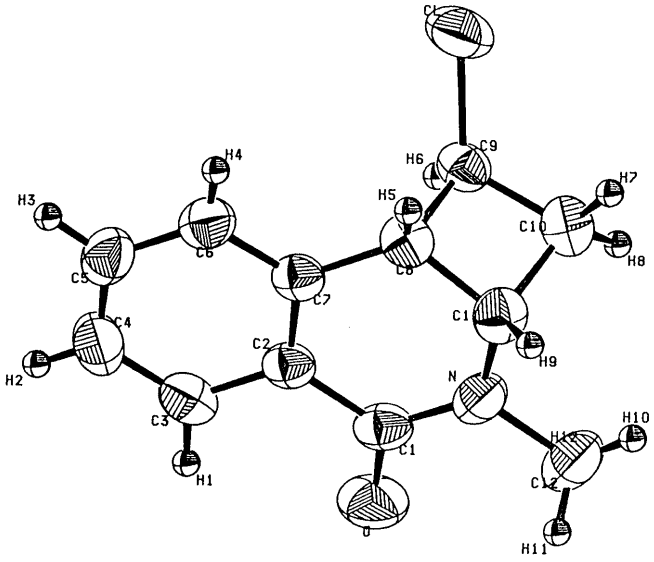


Fig. 2. ORTEP Drawing of the Molecular Structure of **2**A

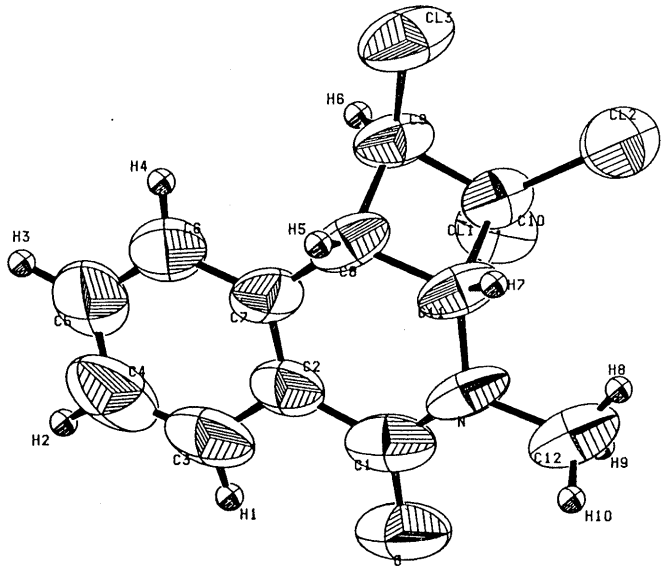


Fig. 4. ORTEP Drawing of the Molecular Structure of **10B**

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 cyclobutisoquinolones as the major products.[7-9] The same regioselectivity was observed in the present study. Thus, when **1** was photoadded 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 cycloadduct (**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-dichloroethylenes 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_3) 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,

TABLE V. Photoaddition of 1-Isoquinolones (**1** and **1'**) to a Variety of Chloroethylenes in Methanol

Entry	Substrate	Chloroethylene	Product (Yields in %)
1	**1**	$ClCH=CH_2$	**2A** (67), **3B** (10)
2	**1'**	The same olefin	**2'A** (50), **3'B** (14)
3	**1**	*cis*-ClCH=CHCl	**4B** (7), **5A** (44)
			6B (10), **7B** (21)
4	**1'**	The same olefin	**4'B** (6), **5'A** (59)
			6'B (4), **7'B** (12)
5	**1**	*trans*-ClCH=CHCl	**4B** (32), **5A** (22)
			6B (17), **7B** (16)
6	**1'**	The same olefin	**4'B** (39), **5'A** (20)
			6'B (14), **7'B** (8)
7	**1**	$CH_2=CCl_2$	**8B** (74), **9B** (9)
8	**1'**	The same olefin	**8'B** (72), **9'B** (11)
9	**1**	$ClCH=CCl_2$	**10B** (32), **11B** (19)
			12B (30), **13B** (13)
10	**1'**	The same olefin	**10'B** (31), **11'B** (18)
			12'B (36), **13'B** (5)

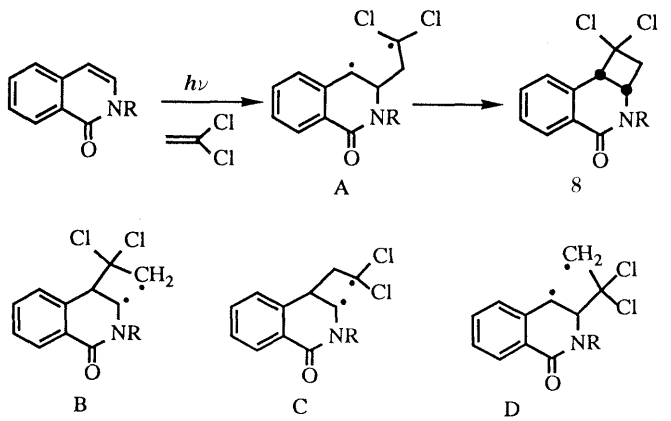


Chart 3

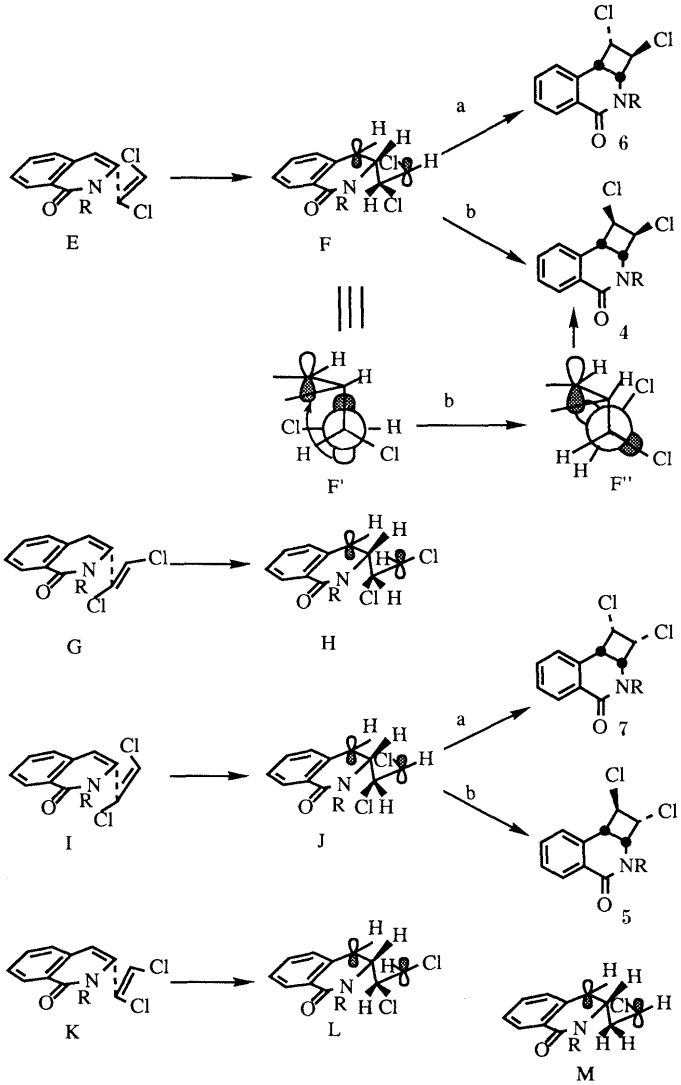


Chart 4

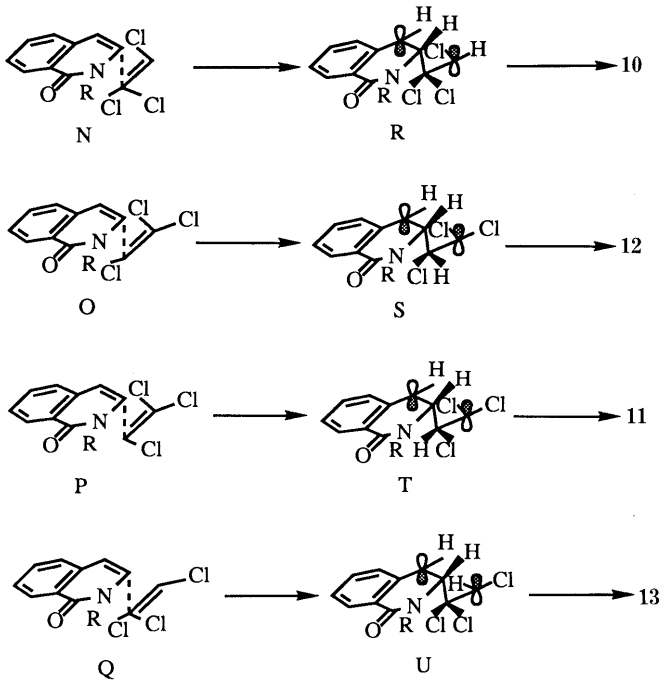


Chart 5

we define the *endo*- and *exo*-approaches of chloroolefins relative to the C-4 position of the isoquinolones (**1** and **1'**)] is 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_{8b} 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 isoquinolones (**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 that, 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 $-\dot{C}HCl$ and $-\dot{C}Cl_2$ radicals do not differ significantly as compared with those of $-\dot{C}HCl$ and $-\dot{C}H_2$ 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_4 of the isoquinolone 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 isoquinolones) 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 is 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 photoadducts (both their relative configurations and conformations) and proposed a mechanism accounting for their formations. Dilling *et al.*[12] as well as Loutfy and de Mayo[13] 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 dioxopyrrolines to a variety of olefins.[14] 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,[15] 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 quinolones to olefins, and also to develop chemical manipulations of the photoadducts 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 isoquinolone ring.[16]

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 ^{1}H-NMR spectra on a JEOL JNM-FX 500 spectrometer, with tetramethylsilane as an internal standard. Mass spectra (MS) were taken with a JEOL JMS-01SG-2 or a JEOL DX-303 spectrometer. Silica gel used for column chromatography was Wakogel C-200, and the ratios of solvent mixtures for chromatography are shown as volume/volume.

Photolyses on a relatively large scale (500 mg—2 g of isoquinolones) 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. Photolyses 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.

Photoreaction of Isoquinolin-1(2*H*)-one (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 g (56%) of (1*S**,2a*S**,8b*S**)-1-chloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut-[*c*]isoquinoline (**2'A**). Further elution with hexane–AcOEt (1:1) gave 342 mg (14%) of (1*R**,2a*S**,8b*S**)-1-chloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**3'B**).

2'A: mp 173—175 °C, colorless needles (acetone–hexane). IR ($CHCl_3$): 3050, 1665 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 2.67 (1H, ddd, J=12.2, 7.2, 7.2 Hz, 2-H_{endo}), 2.75 (1H, ddd, J=12.2, 8.1, 3.4 Hz, 2-H_{exo}), 3.89 (1H, dd, J=8.1, 7.2 Hz, 8b-H), 4.51 (1H, m, 2a-H), 4.52 (1H, ddd, J=8.1, 7.2, 7.2 Hz, 1-H), 6.30 (1H, br s, -NH), 7.29 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.45 (1H, dt, J=1.0, 7.8 Hz), 7.56 (1H, dt, J=1.0, 7.8 Hz), 8.19 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{11}H_{10}ClNO$: 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 ($CHCl_3$): 3046, 1663 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 2.48 (1H, ddd, J=

12.1, 8.3, 8.3 Hz, 2-H_{endo}), 3.05 (1H, dddd, J=12.1, 8.3, 8.3, 3.5 Hz, 2-H_{exo}), 4.16 (1H, ddt, J=8.3, 8.3, 3.8 Hz, 2a-H), 4.26 (1H, ddd, J=8.3, 8.3, 3.5 Hz, 8b-H), 4.66 (1H, dt, J=8.3, 8.3 Hz, 1-H), 6.73 (1H, br s, –NH), 7.26 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.42 (1H, dt, J=1.0, 7.8 Hz), 7.52 (1H, dt, J=1.0, 7.8 Hz), 8.23 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{11}H_{10}ClNO$: C, 63.62; H, 4.85; Cl, 17.07; N, 6.75. Found: C, 63.49; H, 4.94; Cl, 17.30; N, 6.64.

Photoreaction of 2-Methylisoquinolin-1(2*H*)-one (1) with Vinyl Chloride A solution of **1** (318 mg, 12 mmol) and vinyl chloride (7 ml, 0.1 mol) in MeOH (200 ml) was irradiated at >300 nm for 1.5 h. After removal of the solvent, the residue was chromatographed over silica gel (22 g) to give 294 mg (67%) of (1*S**,2a*S**,8b*S**)-1-chloro-3-methyl-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**2A**) from the eluates with hexane–AcOEt (5:1) and 44 mg (10%) of (1*R**,2a*S**,8b*S**)-1-chloro-3-methyl-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**3B**) from the eluates with hexane–AcOEt (3:1).

2A: mp 118—119 °C, colorless prisms (MeOH). IR ($CHCl_3$): 1662 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 2.64 (1H, ddd, J=12.3, 7.2, 7.2 Hz, 2-H_{endo}), 2.86 (1H, ddd, J=12.3, 8.0, 3.2 Hz, 2-H_{exo}), 3.02 (3H, s, –NCH_3), 3.94 (1H, dd, J=8.2, 8.2 Hz, 8b-H), 4.41 (1H, ddd, J=8.2, 7.2, 3.2 Hz, 2a-H), 4.43 (1H, ddd, J=8.2, 8.0, 7.2 Hz, 1-H), 7.22 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.41 (1H, dt, J=1.0, 7.8 Hz), 7.48 (1H, dt, J=1.0, 7.8 Hz), 8.20 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{12}ClNO$: C, 65.02; H, 5.46; Cl, 15.99; N, 6.32. Found: C, 65.29; H, 5.46; Cl, 16.00; N, 6.23.

3B: mp 152—154 °C, colorless prisms (acetone–hexane). IR ($CDCl_3$): 1665 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 2.43 (1H, ddd, J=11.8, 8.1, 8.1 Hz, 2-H_{endo}), 3.03 (3H, s, –NCH_3), 3.12 (1H, dddd, J=11.8, 8.1, 8.1, 2.8 Hz, 2-H_{exo}), 4.08 (1H, dt, J=8.1, 8.1 Hz, 2a-H), 4.29 (1H, ddd, J=8.1, 8.1, 2.8 Hz, 8b-H), 4.65 (1H, dt, J=8.1, 8.1 Hz, 1-H), 7.19 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.42 (1H, dt, J=1.0, 7.8 Hz), 7.52 (1H, dt, J=1.0, 7.8 Hz), 8.28 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{12}ClNO$: C, 65.02; H, 5.46; Cl, 15.99; N, 6.32. Found: C, 65.00; H, 5.64; Cl, 16.16; N, 6.38.

Photoreaction of Isoquinolin-1(2*H*)-one (1′) with *trans*-1,2-Dichloroethylene A solution of **1′** (435 mg, 3 mmol) and *trans*-1,2-dichloroethylene (5.82 g, 60 mmol) in MeOH (300 ml) was irradiated at >300 nm for 3 h. After removal of the solvent, the residue was chromatographed over silica gel (70 g). Elution with hexane–AcOEt (3:1) gave 279 mg (39%) of (1*R**,2*S**,2a*R**,8b*S**)-1,2-dichloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**4′B**). Further elution with the same solvent afforded 246 mg (34%) of a mixture of (1*R**,2*R**,2a*R**,8b*S**)-1,2-dichloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**5′A**) and (1*S**,2*S**,2a*R**,8b*S**)-1,2-dichloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**6′B**) in a ratio of 1.4:1 (as judged from the NMR spectrum). Elution with hexane–AcOEt (1:1) gave 60 mg (8%) of (1*S**,2*R**,2a*R**,8b*S**)-1,2-dichloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**7′B**).

4′B: mp 210—211 °C, colorless needles (acetone–hexane). IR ($CHCl_3$): 3410, 1668 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.14 (1H, ddd, J=9.8, 2.8, 1.6 Hz, 8b-H), 4.51 (1H, m, 2a-H), 4.60 (1H, dd, J=6.2, 2.8 Hz, 1-H), 4.64 (1H, ddd, J=6.2, 6.2, 1.6 Hz, 2-H), 6.38 (1H, br s, –NH), 7.36 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.45 (1H, dt, J=1.0, 7.8 Hz), 7.57 (1H, dt, J=1.0, 7.8 Hz), 8.11 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{11}H_9Cl_2NO$: C, 54.57; H, 3.75; Cl, 29.29; N, 5.79. Found: C, 54.55; H, 3.71; Cl, 29.17; N, 5.71.

A mixture of **5′A** and **6′B** was obtained as colorless crystals: mp 184—187 °C (acetone–hexane). IR ($CHCl_3$): 3400, 1668 cm^{-1}. *Anal.* Calcd $C_{11}H_9Cl_2NO$: C, 54.57; H, 3.75; Cl, 29.29; N, 5.79. Found: C, 54.42; H, 3.79; Cl, 29.30; N, 5.89. The structures and ratio (1.4:1) of **5′A** and **6′B** were determined from the following NMR spectral data ($CDCl_3$: δ 500 MHz):

5′A: 3.65 (1H, dd, J=8.0, 8.0 Hz, 8b-H), 4.42 (1H, dd, J=8.0, 8.0 Hz, 1-H), 4.53 (1H, dd, J=8.0, 6.4 Hz, 2-H), 4.64 (1H, ddd, J=8.0, 6.4, 2.2 Hz, 2a-H), 6.10 (1H, br s, –NH), 7.25 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.46 (1H, dt, J=1.0, 7.8 Hz), 7.54 (1H, dt, J=1.0, 7.8 Hz), 8.21 (1H, dd, J=7.8, 1.0 Hz, 5-H).

6′B: 4.14 (1H, ddd, J=9.5, 7.5, 4.8 Hz, 2a-H), 4.26 (1H, ddd, J=7.5, 7.5, 1.0 Hz, 2-H), 4.34 (1H, ddd, J=9.5, 9.5, 1.0 Hz, 8b-H), 4.54 (1H, dd, J=9.5, 7.5 Hz, 1-H), 6.46 (1H, br s, –NH), 7.31 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.47 (1H, dt, J=1.0, 7.8 Hz), 7.59 (1H, dt, J=1.0, 7.8 Hz), 8.26 (1H, dd, J=7.8, 1.0 Hz, 5H).

7′B: mp 217—218 °C, colorless needles (methanol). IR ($CHCl_3$): 3400, 1662 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.27 (1H, ddd, J=7.2, 7.2, 2.1 Hz, 8b-H), 4.61 (1H, m, 2a-H), 4.94 (1H, ddd, J=7.2, 7.2, 2.1 Hz, 2-H), 5.01 (1H, ddd, J=7.2, 7.2, 2.1 Hz, 1-H), 5.96 (1H, br s, –NH), 7.14 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.46 (1H, dt, J=1.0, 7.8 Hz), 7.54 (1H, dt, J=1.0, 7.8 Hz), 8.23 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{11}H_9Cl_2NO$: C, 54.57; H, 3.75; Cl, 29.29; N, 5.79. Found: C, 54.35; H, 3.84; Cl, 29.18; N, 5.82.

Photoreaction of 1-Isoquinolin-1(2*H*)-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 **4′B**, 153 mg (63%) of a mixture of **5′A** and **6′B** in a ratio of *ca.* 13.5:1, and 30 mg (12%) of **7′B**.

Photoreaction of 2-Methylisoquinolin-1(2*H*)-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–AcOEt (5:1) gave 246 mg (32%) of (1*R**,2*S**,2a*R**,8b*S**)-1,2-dichloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**4B**) and 295 mg (39%) of a mixture of (1*R**,2*R**,2a*R**,8b*S**)-1,2-dichloro-3-methyl-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**5A**) and (1*S**,2*S**,2a*R**,8b*S**)-1,2-dichloro-3-methyl-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**6B**) in a ratio of *ca.* 1.3:1. Elution with hexane–AcOEt (1:1) gave 122 mg (16%) of (1*S**,2*R**,2a*R**,8b*S**)-1,2-dichloro-3-methyl-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**7B**).

4B: mp 182—183 °C, colorless leaves (acetone–hexane). IR ($CHCl_3$): 1665 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.22 (3H, s, –NCH_3), 4.14 (1H, ddd, J=10.4, 3.8, 1.4 Hz, 8b-H), 4.46 (1H, ddd, J=10.4, 7.4, 1.4 Hz, 2a-H), 4.56 (1H, ddd, J=7.4, 3.8, 1.4 Hz, 1-H), 4.66 (1H, ddd, J=7.4, 7.4, 1.4 Hz, 2-H), 7.30 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.42 (1H, dt, J=1.0, 7.8 Hz), 7.52 (1H, dt, J=1.0, 7.8 Hz), 8.22 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{11}Cl_2NO$: C, 56.27; H, 4.33; Cl, 27.68; N, 5.47. Found: C, 56.12; H, 4.44; Cl, 27.33; N, 5.54.

A mixture of **5A** and **6B** was obtained as colorless leaves: mp 113—116 °C (ether–hexane). IR ($CHCl_3$): 1669 cm^{-1}. *Anal.* Calcd for $C_{12}H_{11}Cl_2NO$: C, 56.27; H, 4.33; Cl, 27.68; N, 5.47. Found: C, 55.97; H, 4.32; 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 $CDCl_3$, 500 MHz):

5A: 3.19 (3H, s, NCH_3), 3.82 (1H, dd, J=9.4, 7.4 Hz, 8b-H), 4.26 (1H, ddd, J=7.4, 6.7, 1.4 Hz, 1-H), 4.62 (1H, ddd, J=6.7, 6.7, 1.6 Hz, 2-H), 4.70 (1H, dd, J=9.4, 6.7, 1.4 Hz, 2a-H), 7.21 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.45 (1H, dt, J=1.0, 7.8 Hz), 7.49 (1H, dt, J=1.0, 7.8 Hz, 8.27 (1H, dd, J=7.8, 10 Hz, 5-H).

6B: 3.24 (3H, s, NCH_3), 4.10 (1H, dd, J=9.9, 7.6 Hz, 2a-H), 4.22 (1H, ddd, J=7.6, 7.6, 0.8 Hz, 2-H), 4.34 (1H, ddd, J=9.9, 7.6 Hz, 8b-H), 4.54 (1H, dd, J=7.6, 7.6 Hz, 1-H), 7.21 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.45 (1H, dt, J=1.0, 7.8 Hz), 7.49 (1H, dt, J=1.0, 7.8 Hz), 8.27 (1H, dd, J=7.8, 1.0 Hz, 5-H).

7B: mp 162—163 °C, colorless needles (acetone–hexane). IR ($CHCl_3$): 1662 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.11 (3H, s, –NCH_3), 4.32 (1H, ddd, J=8.8, 8.2, 2.9 Hz, 8b-H), 4.54 (1H, ddd, J=8.8, 5.9, 1.6 Hz, 2a-H), 4.99 (1H, ddd, J=8.2, 5.9, 4 Hz, 2-H), 5.03 (1H, ddd, J=8.2, 8.2, 1.6 Hz, 1-H), 7.13 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.42 (1H, dt, J=1.0, 7.8 Hz), 7.48 (1H, dt, J=1.0, 7.8 Hz), 8.28 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{11}Cl_2NO$: C, 56.27; H, 4.33; Cl, 27.68; N, 5.47. Found: C, 56.07; H, 4.47; Cl, 27.39; N, 5.33.

Photoreaction of 2-Methylisoquinolin-1(2*H*)-one (1) with *cis*-1,2-Dichloroethylene A solution of **1** (318 mg, 2 mmol) and *cis*-1,2-dichloroethylene (3.88 g, 40 mmol) in MeOH (180 ml) was irradiated at >300 nm for 1 h. Work-up as described above gave 37 mg (7%) of **4B**, 273 mg (54%) of a mixture of **5A** and **6B** in a ratio of *ca.* 4.6:1, and 108 mg (21%) of **7B**.

Photoreaction of Isoquinolin-1(2*H*)-one (1′) with 1,1-Dichloroethylene A solution of **1′** (1.74 g, 12 mmol) and 1,1-dichloroethylene (34.5 g, 0.36 mol) in MeOH (1 l) was irradiated at >300 nm for 2.5 h. The residue was chromatographed over silica gel (86 g) to give 318 mg (11%) of (2a*R**,8b*S**)-2,2-dichloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**9′B**) from the eluates with hexane–AcOEt (1:1) and 2.082 g (72%) of (2a*S**,8b*S**)-1,1-dichloro-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**8′B**) from the eluates with hexane–AcOEt (1:2).

8′B: mp 177—179 °C (lit.[7] 175.5—177 °C). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.10 (1H, dd, J=13.5, 4.5 Hz, 2-H_{endo}), 3.46 (1H, ddd, J=13.5, 6.5, 2 Hz, 2-H_{exo}), 4.52 (1H, dddd, J=9, 6.5, 4.5, 2.5 Hz, 2a-H), 4.59 (1H, dd, J=9, 2 Hz, 8b-H), 6.23 (1H, br s, –NH), 7.34 (1H, dd, J=8, 1 Hz, 8-H), 7.50 (1H, dt, J=1, 8 Hz), 7.60 (1H, dt, J=1, 8 Hz), 8.24 (1H, dd, J=8, 1 Hz, 5-H).

9′B: mp 171—173 °C (lit.[7] 168—169 °C). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.03 (1H, ddd, J=13.5, 5.5, 1 Hz, 1-H_{endo}), 3.45 (1H, ddd, J=13.5, 9,

2 Hz, 2-H_{endo}), 4.07 (1H, ddd, J=9.5, 9, 5.5 Hz, 8b-H), 4.74 (1H, dddd, J=9.5, 4, 2, 1 Hz, 2a-H), 6.23 (1H, br s, –NH), 7.11 (1H, dd, J=8, 1 Hz, 8-H), 7.38 (1H, dt, J=1, 8 Hz), 7.51 (1H, dt, J=1, 8 Hz), 8.18 (1H, dd, J=8, 1 Hz, 5-H).

Photoreaction of 2-Methylisoquinolin-1(2*H*)-one (1) with 1,1-Dichloroethylene A solution of **1** (159 mg, 1 mmol) and 1,1-dichloroethylene (2.88 g, 30 mmol) in MeOH (100 ml) was irradiated at 300 nm for 1.5 h. Work-up as described above gave 189 mg (74%) of (2a*S**,8b*S**)-1,1-dichloro-3-methyl-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**8B**) and 23 mg (9%) of (2a*R**,8b*S**)-2,2-dichloro-3-methyl-4-oxo-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**9B**).

8B: mp 127—128 °C (lit.[16] mp 127—128 °C). IR (KBr): 1638 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 2.97 (3H, s, $-NCH_3$), 3.09 (1H, ddd, J=14.2, 4.3, 1.5 Hz, 2-H_{endo}), 3.39 (1H, ddd, J=14.2, 6.7, 2.5 Hz, 2-H_{exo}), 4.32 (1H, ddd, J=8.9, 6.7, 4.3 Hz, 2a-H), 4.57 (1H, ddd, J=8.9, 2.5, 1.5 Hz, 8b-H), 7.23 (1H, dd, J=8.0, 1.0 Hz, 8-H), 7.42 (1H, dt, J=1.0, 8.0 Hz), 7.48 (1H, dt, J=1.0, 8.0 Hz), 8.02 (1H, dd, J=8.0, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{11}Cl_2NO$: C, 56.27; H, 4.33; N, 5.47. Found: C, 56.35; H, 4.05; N, 5.61.

9B: mp 120—121 °C (lit.[16] mp 120—120.5 °C). IR (KBr): 1645 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 2.95 (1H, ddd, J=13.9, 3.6, 1.4 Hz, 1-H_{endo}), 3.16 (3H, s, $-NCH_3$), 3.47 (1H, dd, J=13.9, 9.5 Hz, 1-H_{exo}), 4.04 (1H, ddd, J=10.2, 9.5, 3.6 Hz, 8b-H), 4.72 (1H, dd, J=10.2, 1.4 Hz, 2a-H), 7.05 (1H, dd, J=8.0, 1.0 Hz, 8-H), 7.33 (1H, dt, J=1.0, 8.0 Hz), 7.45 (1H, dt, J=1.0, 8.0 Hz), 8.20 (1H, dd, J=8.0, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{11}Cl_2NO$: C, 56.27; H, 4.33; N, 56.47. Found: C, 56.33; H, 4.18; N, 5.58.

Photoreaction of Isoquinolin-1(2*H*)-one (1′) with Trichloroethylene A solution of **1′** (290 mg, 2 mmol) and trichloroethylene (7.883 g, 60 mmol) in MeOH (200 ml) was irradiated at >300 nm for 2.5 h. The residue was subjected to column cromatography over silica gel (34 g) to give 169 mg (31%) of (1*R**,2a*R**,8b*S**)-4-oxo-1,2,2-trichloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**10′B**) from the eluates with hexane–AcOEt (5:1), 101 mg (18%) of (2*S**,2a*R**,8b*S**)-4-oxo-1,1,2-trichloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**11′B**) from the eluates with hexane–AcOEt (3:1), 28 mg (5%) of (1*S**,2a*R**,8b*S**)-4-oxo-1,2,2-trichloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**13′B**) from the eluates with hexane–AcOEt (2:1), and 200 mg (36%) of (2*R**,2a*R**,8b*S**)-4-oxo-1,1,2-trichloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**12′B**) from the eluates with hexane–AcOEt (1:1).

11′B: mp 254.5—256 °C, colorless needles (acetone–hexane). IR (Nujol): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.37 (1H, ddd, J=9.8, 7.7, 4.0 Hz, 2a-H), 4.61 (1H, dd, J=7.7, 1.6 Hz, 2-H), 4.63 (1H, dd, J=9.8, 1.6 Hz, 8b-H), 6.31 (1H, br s, –NH), 7.48 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.52 (1H, dt, J=1.0, 7.8 Hz), 7.65 (1H, dt, J=1.0, 7.8 Hz), 8.26 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{11}H_8Cl_3NO$: C, 47.77; H, 2.92; Cl, 38.46; N, 5.06. Found: C, 47.69; H, 2.82; Cl, 38.17; N, 5.04.

12′B: mp 219—221 °C, colorless needles (acetone–hexane). IR (Nujol): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.46 (1H, dd, J=8.0, 1.8 Hz, 8b-H), 4.67 (1H, ddd, J=8.0, 5.9, 1.9 Hz, 2a-H), 5.09 (1H, dd, J=5.9, 1.8 Hz, 2-H), 5.90 (1H, br s, –NH), 7.32 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.53 (1H, dt, J=1.0, 7.8 Hz), 7.61 (1H, dt, J=1.0, 7.8 Hz), 8.23 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{11}H_8Cl_3NO$: C, 47.77; H, 2.92; Cl, 38.46; N, 5.06. Found: C, 47.89; H, 2.86; Cl, 38.59; N, 5.02.

10′B: mp 182.5—184 °C, colorless needles (acetone–hexane). IR (Nujol): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.94 (1H, dd, J=8.8, 8.8 Hz, 8b-H), 4.71 (2H, m, 1′-H, 2a-H), 6.30 (1H, br s, –NH), 7.26 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.48 (1H, dt, J=1.0, 7.8 Hz), 7.57 (1H, dt, J=1.0, 7.8 Hz), 8.22 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{11}H_8Cl_3NO$: C, 47.77; H, 2.92; Cl, 38.46; N, 5.06. Found: C, 48.05; H, 2.82; Cl, 38.46 N, 5.08.

13′B: mp 181—183 °C, colorless needles (acetone–hexane). IR (Nujol): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.37 (1H, dd, J=10.6, 9.3 Hz, 8b-H), 4.77 (1H, ddd, J=10.6, 4.4, 1.2 Hz, 2a-H), 5.14 (1H, dd, J=9.3, 1.2 Hz, 1-H), 6.43 (1H, br s, –NH), 7.19 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.46 (1H, dt, J=1.0, 7.8 Hz), 7.55 (1H, dt, J=1.0, 7.8 Hz), 8.23 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{11}H_8Cl_3NO$: C, 47.77; H, 2.92; Cl, 38.46; N, 5.06. Found: C, 48.03; H, 2.89; Cl, 38.33; N, 5.22.

Photoreaction of 2-Methylisoquinolin-1(2*H*)-one (1) with Trichloroethylene A solution of **1** (477 mg, 3 mmol) and trichloroethylene (11.7 g, 90 mmol) in MeOH (230 ml) was irradiated at >300 nm for 2 h. Work-up as described above gave 249 mg (32%) of (1*R**,2a*R**,8b*S**)-3-methyl-4-oxo-1,2,2-trichloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**10B**) from the eluates with hexane–AcOEt (7:1), 165 mg (19%) of (2*S**,2a*R**,8b*S**)-3-methyl-4-oxo-1,1,2-trichloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**11B**) from the eluates with hexane–AcOEt (5:1), 106 mg (13%) of (1*S**,2a*R**,8b*S**)-3-methyl-4-oxo-1,2,2-trichloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**13B**) from the eluates with hexane–AcOEt (3:1), and 260 mg (30%) of (2*R**,2a*R**,8b*S**)-3-methyl-4-oxo-1,1,2-trichloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**12B**) from the eluates with hexane–AcOEt (1:1).

10B: mp 110—111 °C, colorless needles (hexane). IR ($CHCl_3$): 1671 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.27 (3H, s, $-NCH_3$), 4.07 (1H, dd, J=10.6, 5.4 Hz, 8b-H), 4.62 (1H, dd, J=5.4, 1.2 Hz, 1-H), 4.82 (1H, dd, J=10.6, 1.2 Hz, 2a-H), 7.22 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.43 (1H, dt, J=1.0, 7.8 Hz), 7.53 (1H, dt, J=1.0, 7.8 Hz), 8.24 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{10}Cl_3NO$: C, 49.60; H, 3.47; Cl, 36.60; N, 4.82. Found: C, 49.66; H, 3.57; Cl, 36.68; N, 4.94.

11B: mp 139.5—140.5 °C, colorless leaves (ether). IR ($CHCl_3$): 1668 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.24 (3H, s, $-NCH_3$), 4.33 (1H, dd, J=9.7, 7.3 Hz, 2a-H), 4.60 (1H, dd, J=7.3, 1.3 Hz, 2-H), 4.63 (1H, dd, J=9.7, 1.3 Hz, 8b-H), 7.41 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.50 (1H, dt, J=1.0, 7.8 Hz), 7.59 (1H, dt, J=1.0, 7.8 Hz), 8.28 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{10}Cl_3NO$: C, 49.60; H, 3.47; Cl, 36.60 N, 4.82. Found: C, 49.61; H, 3.24; Cl, 36.69; N, 4.75.

12B: mp 171—172 °C, colorless leaves (acetone–hexane). IR ($CHCl_3$): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.16 (3H, s, $-NCH_3$), 4.57 (1H, dd, J=9.0, 2.5 Hz, 8b-H), 4.79 (1H, dd, J=9.0, 6.0 Hz, 2a-H), 5.13 (1H, dd, J=6.0, 2.5 Hz, 2-H), 7.22 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.43 (1H, dt, J=1.0, 7.8 Hz), 7.53 (1H, dt, J=1.0, 7.8 Hz), 8.24 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{10}Cl_3NO$: C, 49.60; H, 3.47; Cl, 36.60; N, 4.82. Found: C, 49.38; H, 3.37; Cl, 36.88; N, 4.80.

13B: mp 176—178 °C, colorless leaves (hexane). IR ($CHCl_3$): 1669 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.29 (3H, s, $-NCH_3$), 4.34 (1H, dd, J=9.9, 9.8, 8b-H), 4.72 (1H, d, J=9.9 Hz, 2a-H), 5.14 (1H, d, J=9.8 Hz, 1-H), 7.13 (1H, dd, J=7.8, 1.0 Hz, 8-H), 7.42 (1H, dt, J=1.0, 7.8 Hz), 7.51 (1H, dt, J=1.0, 7.8 Hz), 8.24 (1H, dd, J=7.8, 1.0 Hz, 5-H). *Anal.* Calcd for $C_{12}H_{10}Cl_3NO$: C, 49.60; H, 3.47; Cl, 36.60; N, 4.82. Found: C, 49.63; H, 3.40; Cl, 36.50; N, 4.82.

Photoreaction of Isoquinolin-1(2*H*)-one (1′) with Tetrachloroethylene A solution of **1′** (87 mg, 0.6 mmol) and tetrachloroethylene (9.95 g, 60 mmol) in MeOH (70 ml) was irradiated for 3.25 h. The residue was purified by recrystallization from acetone–hexane to give 111 mg (60%) of (2a*R**,8b*S**)-4-oxo-1,1,2,2-tetrachloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**14′B**).

14′B: mp 228—229 °C, colorless needles (acetone–hexane). IR (Nujol): 1675 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 4.93—5.07 (2H, m, 2a-H, 8b-H), 7.30—7.80 (3H, m, aromatic H), 7.98—8.18 (1H, m, 5-H), 8.73—9.02 (1H, br s, –NH). *Anal.* Calcd for $C_{11}H_7Cl_4NO$: C, 42.48; H, 2.27; Cl, 45.60; N, 4.50. Found: C, 42.31; H, 2.18; Cl, 45.88; N, 4.61.

Photoreaction of 2-Methylisoquinolin-1(2*H*)-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 (2a*R**,8b*S**)-3-methyl-4-oxo-1,1,2,2-tetrachloro-1,2,2a,3,4,8b-hexahydrocyclobut[*c*]isoquinoline (**14B**) from the eluates with hexane–AcOEt (1:3).

TABLE VI. Crystal Data[17]

Compd.	**2A**	**4′B**	**10B**
Crystal system	Monoclinic	Triclinic	Monoclinic
Lattice parameters			
a (Å)	8.114 (2)	8.978 (4)	10.712 (2)
b (Å)	14.649 (2)	9.610 (3)	8.347 (2)
c (Å)	9.679 (4)	6.917 (2)	14.042 (2)
α (°)	—	106.84 (2)	—
β (°)	111.46 (2)	95.24 (3)	101.81 (1)
γ (°)	—	64.48 (2)	—
V (Å^3)	1070.8 (5)	515.1 (3)	1228.9 (4)
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/a$
Z value	4	2	4
D_C (g/cm^3)	1.38	1.56	1.57
Number of reflections used for calculation ($>3\sigma$ (I))	1669	1189	816
R value	0.053	0.053	0.041

14B: mp 148—149 °C, colorless prisms (ether). IR ($CHCl_3$): 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.23 (3H, s, $-NCH_3$), 4.65 (1H, d, J=10 Hz, 8-H), 4.95 (1H, d, J=10 Hz, 2a-H), 7.21 (3H, m, aromatic H), 7.99 (1H, m, 5-H). *Anal.* Calcd for $C_{12}H_9Cl_4NO$: 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] Reflection data were collected on a Rigaku AFC-5R four-circle diffractometer controlled by the MSC/AFC program package, using Mo K_α radiation monochromated by a graphite monochromator, in the 2θ–ω scan mode. Reflections 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**, **4'B**, and **10B** are given in Table VI.

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