

## The Photocycloaddition of Carbostyryl to Olefins. The Stereochemistry of the Adducts

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The photocycloaddition of carbostyryl to olefins gives a series of dihydrocyclobuta[c]-2-quinolones in a regio-specific manner. The stereochemistry of these products indicates that the reaction proceeds to form selectively the head-to-tail adducts.

Cyclic enone photocycloaddition to olefins has been used extensively for the synthesis of cyclobutanes<sup>2</sup> and has provided the means for synthesis of cubane,<sup>3a</sup> atisine,<sup>3b</sup> bourbonenes,<sup>4</sup> caryophyllenes,<sup>5</sup>  $\beta$ -himachalene,<sup>6</sup> and a variety of other natural products<sup>7</sup> and extremely novel structures.<sup>2</sup> We have investigated the photocycloaddition of carbostyryls **1** (cyclohexene heteroanalog) to olefins because of its utility in synthesis of the unique tricyclic system **2**.

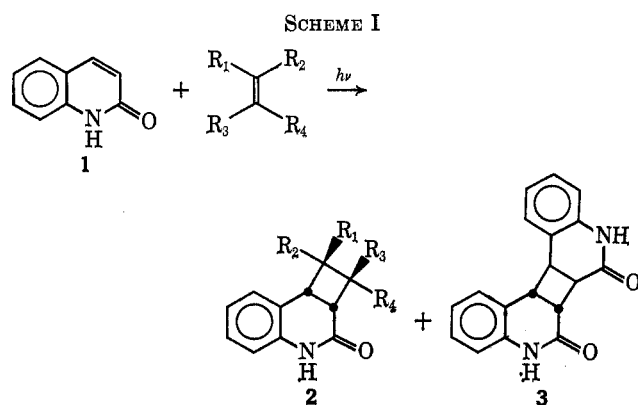
The cyclobutane derivatives of carbostyryls are readily synthesized photochemically without the aid of sensitizers in good to excellent yields. Carbostyryl dimerization usually accompanies the cycloaddition reaction, and the yield of dimer is dependent on concentration, solvent, and olefin. A series of adducts was prepared from carbostyryls and olefins and is described in Scheme I. In general, a ratio of 10 equiv of olefin to 1 equiv of carbostyryl was used at various concentra-

tions in ethanol or *N,N'*-dimethylacetamide. Reactions were followed by tlc and usually run to completion. The results are summarized in Table I.

TABLE I

Compd	Concn of 1 <sup>a</sup>	Solvent	Irradn time, <sup>b</sup> hr	Yield of adduct, %	Yield of dimer <b>3</b> , %
2a	69	Ethanol	20	90	9.4
2b	69	Ethanol	72	57	40
2c	41	Ethanol	72	50	50
2d	0.69	Dimethylacetamide	24	100	0
2e	69	Ethanol	144	65	35
2f	50	Ethanol	96	63	37
2g	69	Ethanol	72	8	22
2h	69	Ethanol	48	79	20
2i	50	Dimethylacetamide	96	71	5
2j	6.9	Ethanol	192	20	20
2k	69	Ethanol	72	54	46
2l	69	Ethanol	144	49	43

<sup>a</sup> Concentration of  $1 \times 10^{-3}$  M. <sup>b</sup> Irradiation time for a total volume of 700 ml of solvent irradiated in the Rayonet apparatus with 16 black-light lamps.



- a, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = CH<sub>3</sub>  
 b, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>; R<sub>3</sub> = R<sub>4</sub> = H  
 c, R<sub>1</sub> = R<sub>2</sub> = CH<sub>2</sub>CH<sub>3</sub>; R<sub>3</sub> = R<sub>4</sub> = H  
 d, R<sub>1</sub> = R<sub>2</sub> = OCH<sub>3</sub>; R<sub>3</sub> = R<sub>4</sub> = H  
 e, R<sub>1</sub> = OCH<sub>3</sub>; R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
 f, R<sub>1</sub> = CN; R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
 g, R<sub>1</sub> = OCOC<sub>2</sub>H<sub>5</sub>; R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
 h, R<sub>1</sub> = O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>; R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
 i, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = Cl  
 j, R<sub>1</sub> = R<sub>2</sub> = Ph; R<sub>3</sub> = R<sub>4</sub> = H  
 k, R<sub>1</sub> = R<sub>3</sub> = -CH<sub>2</sub>-3; R<sub>2</sub> = R<sub>4</sub> = H  
 l, R<sub>1</sub> = R<sub>3</sub> = -CH<sub>2</sub>-6; R<sub>2</sub> = R<sub>4</sub> = H

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We have already presented some evidence to support the assigned structures **2** in a preliminary communication.<sup>8</sup> In addition, Loev, *et al.*,<sup>9</sup> have described similar products from 6-trifluoromethyl-*N*-methylcarbostyryl and olefins, and Buchardt<sup>10</sup> has observed results related to ours. The photochemical dimerization of **1**,<sup>11</sup> *N*-methylcarbostyryl,<sup>11</sup> and 6-trifluoromethyl-*N*-methylcarbostyryl<sup>9</sup> has been described, and the stereochemistry of the dimers has been elegantly elucidated.<sup>11</sup>

Besides the elemental analyses, which are summarized in Table II, our evidence for the cycloadducts is based mainly on spectral data. The ir lactam carbonyl band of **2a** is in reasonable agreement with that of 3,4-dihydrocarbostyryl (1671 and 1675 cm<sup>-1</sup>,<sup>12</sup> respectively, Nujol mull). The uv maximum of **2a** [ $\lambda_{\max}^{\text{EtOH}}$  259 m $\mu$  ( $\epsilon$  8600)] is shifted to lower frequency from that of 3,4-dihydrocarbostyryl [ $\lambda_{\max}^{\text{EtOH}}$  250 m $\mu$  ( $\epsilon$  12,000)].<sup>12</sup> The ir and uv spectra of the other cycloadducts (**2**) also exhibit these shifts to lower frequency, and similar data were observed by Buchardt for the dimers **3** [ $\lambda_{\max}^{\text{dioxane}}$  259 m $\mu$  ( $\log \epsilon$  4.23)].<sup>11b</sup>

The mass spectra of the adducts exhibit weak parent molecule ions; the major ion is consistently due to

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TABLE II  
 ELEMENTAL ANALYSES OF CYCLOADDUCTS

Compd	Adduct formula	Carbon		Hydrogen		Nitrogen		Oxygen	
		Calcd, %	Found, %	Calcd, %	Found, %	Calcd, %	Found, %	Calcd, %	Found, %
2a	C <sub>15</sub> H <sub>19</sub> NO	78.56	78.39	8.35	8.39	6.11	6.13	6.98	7.08
2b	C <sub>13</sub> H <sub>15</sub> NO	77.58	77.60	7.51	7.55	6.96	7.27	7.95	8.17
2c	C <sub>15</sub> H <sub>19</sub> NO	78.56	78.53	8.35	8.35	6.11	6.07		
2d	C <sub>13</sub> H <sub>15</sub> NO <sub>3</sub>	66.93	66.96	6.48	6.41	6.01	5.86	20.58	20.85
2e	C <sub>12</sub> H <sub>13</sub> NO <sub>2</sub>	70.91	71.03	6.45	6.50	6.89	7.04	15.75	15.97
2f	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O	72.71	72.67	5.09	4.98	14.13	13.97		
2g	C <sub>13</sub> H <sub>13</sub> NO <sub>3</sub>	67.52	67.53	5.67	5.62	6.06	6.03		
2h	C <sub>15</sub> H <sub>19</sub> NO <sub>2</sub>	73.44	73.30	7.81	7.88	5.71	5.82	13.04	13.12
2i	C <sub>11</sub> H <sub>7</sub> NOCl <sup>a</sup>	42.48	42.60	2.27	2.20	4.50	4.59		
2j	C <sub>23</sub> H <sub>19</sub> NO	84.89	84.85	5.89	5.60	4.30	4.33		
2k	C <sub>14</sub> H <sub>15</sub> NO	78.84	78.89	7.09	7.12	6.57	6.33	7.50	7.51
2l	C <sub>17</sub> H <sub>21</sub> NO	79.96	80.30	8.29	8.42	5.49	5.14		

<sup>a</sup> Calcd: Cl, 45.59. Found: Cl, 45.45.

carbostyryl (*m/e* 145) from the loss of photocycloaddled olefin.

The most compelling evidence for the assigned structure is given by the nmr spectra. For example, the spectrum of 2a (CDCl<sub>3</sub>, TMS) has four methyl singlets at  $\delta$  0.83, 1.13, 1.32, and 1.36, four aromatic hydrogens at  $\delta$  7.13 (m), and an AB pattern for the C-3 and C-6 cyclobutane hydrogens at  $\delta$  3.40 and 3.57 ( $J_{AB} = 10.3$  Hz), respectively. The large coupling constant is consistent with *cis* vicinal hydrogens in a rigid cyclobutane ring, and would therefore indicate *cis* ring fusion.<sup>13</sup>

*trans* ring fusion of six- and four-membered rings has been observed in photochemical cycloadditions of cyclohexenone<sup>14a</sup> and 4,4-dimethylcyclohexenone.<sup>14b</sup> It was also observed in 6-4 and 5-4 fused-ring systems of cyclohexadiene and cyclopentadiene with dichloromaleic anhydride.<sup>15</sup> However, the coupling of an intermediate biradical leading to *trans* ring juncture is less probable in our system because of the steric constraints of the fused benzene ring and the amide function.

The stereochemical assignment of substituents on cyclobutane rings by nmr is untenable when it is based purely on the supposition that *cis* vicinal coupling constants will be larger than *trans*. In many cases  $J_{cis} \cong J_{trans}$  owing to fast conformational averaging, and in other cases they are nearly equivalent owing to puckering in the molecule that significantly alters the vicinal dihedral angles from 0° (*cis*) and 120° (*trans*),<sup>13</sup> or to fast conformational averaging. A good example of this phenomenon is found in the nmr spectrum of anemonin, which has two  $J_{cis}$  values of 10.2 Hz, a  $J_{trans}$  value of 10.7 Hz, and a  $J_{trans}$  value of 2.2 Hz.<sup>16</sup> However, in cases of rigid, planar cyclobutanes, the *cis* vicinal coupling constants have been shown to be significantly larger than the *trans*; e.g., cyclobutanone is reported to have a  $J_{cis}$  value of 10.02 Hz and a  $J_{trans}$  value of 6.35 Hz.<sup>17</sup>

Structure assignment on the basis of size of coupling

constants has been used by others,<sup>18</sup> but in view of the above controversy over *cis* and *trans* couplings we attempted to further corroborate our *cis* assignment. In the photoaddition of 4,4-dimethylcyclohex-2-enone to dimethyl ketene acetal, Chapman, *et al.*,<sup>19</sup> found that both *cis* and *trans* ring-fusion products were obtained. They were able to convert the kinetically formed *trans* adduct into the thermodynamically more stable *cis* product with base.

By analogy, if 2a had a *trans* ring juncture, treatment with base should give the *cis* ring-fused product. Compound 2a was treated with 3.5 equiv of *n*-butyllithium and 1,4-diazabicyclo[2.2.2]octane in tetrahydrofuran at 0°. After 2.5 hr half of the reaction was quenched with H<sub>2</sub>O and half with D<sub>2</sub>O. The reaction mixtures were separated by column chromatography, and the fractions corresponding to 2a were analyzed by nmr. The nmr of the adduct from the D<sub>2</sub>O treatment indicated 100% D incorporation (the cyclobutane hydrogen AB pattern of 2a was replaced by a single, somewhat broad, resonance line at  $\delta$  3.58 corresponding to the C-6 hydrogen). The nmr spectrum of the adduct from the H<sub>2</sub>O treatment was identical with that of the starting material 2a. This evidence strongly supports the supposition of *cis* ring fusion for 2a and presumably for other adducts 2.

In the compounds described below, which are specific examples of adducts obtained from unique types of olefins, we will discuss the nmr spectra in detail. This is necessary because of the aforementioned controversy over nmr data of cyclobutane rings, and because there is only limited analysis of these systems reported to date.<sup>8,9,11,18</sup>

The structure of adducts from unsymmetrical 1,1-disubstituted olefins is not immediately predictable, since both head-to-head (2m, R<sub>1</sub> = R<sub>2</sub> = H; R<sub>3</sub> = R<sub>4</sub> = CH<sub>3</sub>) and head-to-tail (2b, R<sub>3</sub> = R<sub>4</sub> = H; R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>) adducts could be expected. In the pioneering work on photocycloaddition of cyclohexenones to unsymmetrical olefins, Corey, *et al.*,<sup>14</sup> observed a 3:1 preference for head-to-tail over head-to-head products from cyclohexenone and isobutylene. Thus it is quite reasonable to expect a mixture of isomers from the irradiation of carbostyryls with similar olefins. However, after careful analysis by vpc, tlc, and nmr, we were not able to detect the presence of more than one isomer from

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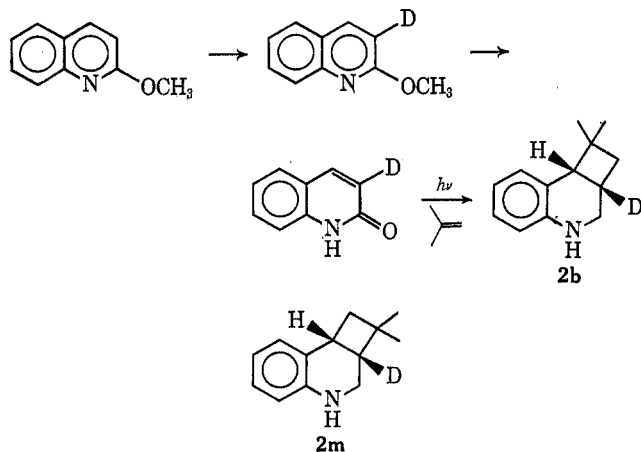
the photoaddition of any carbostyryl to a 1,1-disubstituted olefin.

The 60-MHz nmr spectrum of the isobutylene carbostyryl cycloadduct **2b** is quite complex; in  $\text{CF}_3\text{CO}_2\text{D}$  the methylene and methine cyclobutane hydrogens are broad multiplets at  $\delta$  2.38 (2 H) and 3.5 (2 H), respectively. The compound was analyzed on a 220-MHz instrument and a simple first-order spectrum in  $\text{CDCl}_3$  (TMS) for the four-proton system was obtained; the specific chemical shifts and coupling constants are tabulated in Table III, on the basis of which we tentatively assigned structure **2b**.

TABLE III  
220-MHz NMR DATA ( $\text{CDCl}_3$ ) FOR **2b**

H	$\delta$ , ppm	$J$ , Hz		
		4- <i>exo</i>	4- <i>endo</i>	6
3	3.35	10.0	4.5	10.0
4- <i>exo</i>	2.49		-12.0	
4- <i>endo</i>	2.21			
6	3.50			

Further proof was obtained by preparation of C-3 deuterium-labeled carbostyryl from 2-methoxyquinoline by treatment with *n*-butyllithium and  $\text{D}_2\text{O}$  followed by acid hydrolysis. The photocycloaddition of the 3-deuteriocarbostyryl to isobutylene gave the 3-deuterio-6-hydrocyclobuta[*c*]-2-quinolone. The nmr spectrum ( $\text{CF}_3\text{CO}_2\text{D}$ ) of the cyclobutane hydrogens was a simple



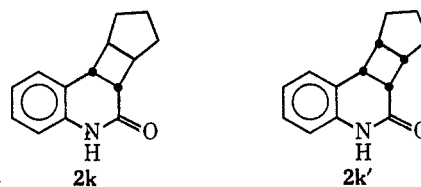
ABM pattern: a singlet at  $\delta$  3.68 (1 H) and a quartet at  $\delta$  2.33 and 2.68 (2 H,  $J_{AB} = 12.1$  Hz). Double-resonance nmr experiments indicated that cross-ring coupling was present:  $|J_{6,4\text{-}exo}| = 0.84$  Hz and  $|J_{6,4\text{-}endo}| = 0.68$  Hz. These values are of opposite sign, but it was not possible to determine the absolute value of each. In addition, the low-field methylene proton is weakly coupled ( $0.5 \text{ Hz} > J > 0.0 \text{ Hz}$ ) with the high-field methyl group. This spectrum is compatible only with the head-to-tail adduct **2b**; the head-to-head isomer **2m** would be expected to have larger coupling constants for the vicinal hydrogens ( $J_{AM}, J_{BM} \cong 6\text{--}10$  Hz), producing a more complex ABM pattern than that observed ( $J_{AM}, J_{BM} < 1$  Hz).

In addition it was possible to exchange the C-3 hydrogen of certain adducts for deuterium by treating them with butyllithium-DABCO and quenching with  $\text{D}_2\text{O}$  as described above. The nmr of the product from this treatment of **2b** after purification by chromatography was identical with that obtained from the photocyclo-

addition reaction of 3-deuteriocarbostyryl and isobutylene. By this deuterium-labeling method we were able to simplify the four-proton nmr spectra of other 1,1-disubstituted adducts to a three-spin system and thereby confirm the head-to-tail photochemical addition. Furthermore, this method of incorporation of deuterium offers a more convenient alternative to the aforementioned synthesis of 3-deuteriocarbostyryl.

By first approximation, cycloalkenes should give *syn* and *anti* fused-ring products on reaction with carbostyryl. However, in view of carbostyryl's dimerization to a single head-to-head *anti* ring-fused product, we expected to observe a single product from cyclopentene or cyclooctene addition.

The product **2k** from irradiation of **1** and cyclopentene appeared to be one product from vpc, tlc, and nmr data. The A-60 nmr spectrum was quite complex and the stereochemistry of the product was not known. However, the 220-MHz nmr spectrum ( $\text{CDCl}_3$ ) not only helped elucidate the structure but also indicated the presence of two isomers in the reaction mixture: the *anti* ring-fused adduct **2k** and the *syn* adduct **2k'** in a



3:1 ratio. The 220-MHz nmr data are presented in Table IV.

TABLE IV  
220-MHz NMR DATA ( $\text{CDCl}_3$ ) FOR **2k** AND **2k'**

H	$\delta$ , ppm	$J$ , Hz				H	$\delta$ , ppm	$J$ , Hz		
		4	8	9	5-7			4	8	9
3	2.88	4.5		9.7	0	3	3.92	10.5		10.5
4	3.10		7		7.0	4	3.36		10.5	
8	2.72			4.5	7.0	8	3.3			10.5
9	3.21				0	9	4.00			
5/7	1.92									

The four cyclobutane hydrogens of **2k** were readily identifiable by first-order analysis: H-3 and H-9 formed a four line pattern—a doublet of doublets—with  $J$  values of 4.5 and 9.7 Hz; H-4 and H-8 gave a six-line pattern—two sets of triplets each—with  $J$  values of 4.5, 7.0, and 7.0 Hz.

The structure **2k'** was assigned on the basis of the low-field triplets of H-3 and H-9 with the large  $J$  values of 10.5 Hz. This is consistent with four *cis* hydrogens on a cyclobutane ring. The upfield proton H-4 (or H-8) was further split by *ca.* 7 Hz by the methylene hydrogens C-5 and C-7. Part of the H-8 (or H-4) resonance signal was masked by H-9 of **2k**, and a complete analysis is not possible.

In view of the data from cyclopentene addition, one could expect, with monosubstituted unsymmetrical olefins, not one head-to-tail adduct, but a mixture<sup>20</sup> of two isomers with *exo* and *endo* substituents. The photocycloaddition of carbostyryl to vinyl methyl ether should produce epimers (*exo*- and *endo*-methoxy) and possibly isomers owing to direction of addition (4- or

(20) This is consistent with our vpc data for adducts with these olefins; however, the cyclopentene adduct gave one peak in the vpc.

5-methoxy from head-to-head or head-to-tail addition) and type of ring fusion (*cis* or *trans* at C-3 and C-6). Only *exo*-5- and *endo*-5-methoxy epimers with a *cis* fused-ring juncture were found. This might be expected in that vinyl methyl ether should react similarly to dimethyl ketene acetal and give the *cis* ring-fused, head-to-tail products. However, acrylonitrile could give either the 5- or 4-cyano mixture depending on the preferred reaction mechanism. A biradical intermediate would favor a 5-cyano mixture, while a dipole-dipole interaction mechanism favors the 4-cyano mixture.

The irradiation of **1** with vinyl methyl ether, followed by subsequent removal of dimer and chromatography, gave the mixture **2e** in 33% yield. The analysis of the 220-MHz nmr spectrum revealed a 56:44 mixture of the *exo*- to *endo*-5-methoxy adducts. After three recrystallizations from acetone, the pure *exo*-5-methoxy-3,6-dihydrocyclobuta[*c*]-2-quinolone was obtained in 4% yield. The main support for the proposed structure is the nmr data of the pure isomer presented in Table V.

TABLE V  
220 MHz NMR DATA (CDCl<sub>3</sub>) FOR *exo*-**2e**

H	$\delta$ , ppm	$J$ , Hz			
		4- <i>endo</i>	4- <i>exo</i>	5- <i>endo</i>	6
3	3.26	3.0	10.0	1.5	10.0
4- <i>endo</i>	2.78		12.0	7.0	1.0
4- <i>exo</i>	2.54			7.0	
5- <i>endo</i>	4.04				7.0
6	3.64				

The five cyclobutane hydrogens are readily identifiable by their first-order patterns: H-6 is a doublet of doublets that is coupled to the *cis* vicinal H-3 by 10.0 Hz and to the *trans* vicinal H-5 by 7.0 Hz; H-3 is a triplet with one portion masked by the OCH<sub>3</sub> at 3.30 ppm and the other two resonances further split by 3.0 and 1.5 Hz; H-5 is a quartet with 7.0-Hz splitting and with secondary splitting of 1.5 Hz; H-4 *exo* is a triplet of doublets (the center lines of the quartet are split by 3.0 Hz); and H-4 *endo* is a somewhat complex 16-line pattern incorporating all of the observed  $J$  values.

The assignment of the head-to-tail structure is strongly supported by deuterium-exchange experiments and the nmr spectra. The assignment of the *exo* position for the methoxy group is consistent with the expectation that the major epimer of the reaction mixture should have this configuration. Further support can be obtained from the magnitude of the  $^3J_{vic}$  for the H-3, H-4, and H-5 hydrogens. A thorough analysis<sup>21</sup> of this system supports the puckered form of the cyclobutane ring, allowing the methoxyl group to assume the equatorial position.

We have not been able to separate the isomers by chromatography and have had to rely on the nmr of the mixture to confirm the identity of the other isomer. There is considerable overlap between the resonance signals of the two isomers, and a complete analysis of the minor product (*endo*-5-methoxy) is not possible.

The irradiation of carbostyryl and acrylonitrile gave a considerable amount of dimer (37%) and some adduct **2f** (42%). We have been able to isolate the lower  $R_f$  isomer (on silica gel tlc) by recrystallization from

ethanol in 16% yield. Based on the 220-MHz spectrum, we have assigned the cyano group the 5-*endo* position (see Table VI).

TABLE VI  
220-MHz NMR DATA (DMSO-*d*<sub>6</sub>) FOR THE  
*endo*-5-CYANO ISOMER **2f**

H	$\delta$ , ppm	$J$ , Hz			
		4- <i>exo</i>	4- <i>endo</i>	5- <i>exo</i>	6
3	3.38	9.0	6.5	1.0	9.0
4- <i>exo</i>	2.89		12.0	9.0	1.5
4- <i>endo</i>	2.38			6.5	1.0
5- <i>exo</i>	3.85				9.0
6	4.15				

Four of the five cyclobutane hydrogens are readily identifiable by their first-order patterns: H-5 *exo* is masked by protons in the solvent; H-6 is a broad triplet ( $W_{1/2} = 4$  Hz) at  $\delta$  4.15; H-3 is an imperfect quartet at  $\delta$  3.85 with secondary splitting; H-4 *exo* is also an imperfect quartet with secondary splitting; and H-4 *endo* is a doublet of triplets with some overlap to give a five-line pattern.

A more thorough discussion of the nmr of **2f** has been presented elsewhere.<sup>21</sup> The observed coupling constants for H-3, H-4, and H-5 are consistent with the assignment of the 5-cyano group to an equatorial position on a puckered cyclobutane ring.

Although we have not been able to isolate the other isomer, an analysis of the 220-MHz nmr spectrum of the reaction mixture indicates a 40:60 mixture of *exo*- to *endo*-5-cyano-3,6-dihydrocyclobuta[*c*]-2-quinolone. This 40:60 ratio of *exo* to *endo* epimers is inconsistent with what one would expect for a bulky substituent based on the vinyl methyl ether case.

Recently, it was reported<sup>22</sup> that the acetophenone-photosensitized cycloaddition of indene to acrylonitrile gave a 50:45 ratio of *exo*- to *endo*-7-cyano-2,3-benzobicyclo[3,2,0]hept-2-ene. Direct irradiation of either isomer gave a photostationary state composed of a 45:55 *exo*- to *endo*-7-cyano mixture. Equilibrium studies with *t*-butoxide found a 70:30 *exo*- to *endo*-cyano ratio at 25°. These variations in ratio, although small, discount the steric influence of the cyano group.

In view of these results, any interpretation of our data at this time would indicate our lack of understanding of the reaction mechanism, including the specific function of the substituent on the olefin. However, one comment can be made about the mechanism at this time. Since the 5-cyano and not the 4-cyano epimer mixture was obtained, the nature of the product would seem to be determined by "the more stable biradical intermediate" theory and not by a dipole-dipole interaction mechanism. Further information on the mechanism of photocycloaddition will be published at a later date.

### Experimental Section

Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. Ultraviolet spectra were taken on a Cary 14 recording spectrophotometer. In general, nmr spectra were obtained on a Varian Associates A-60 spectrometer. All 220-MHz nmr spectra were run by Varian Associates, Palo Alto, Calif.

(21) E. B. Whipple, Jr., and G. R. Evanega, *Org. Magnetic Resonance*, **2**, 1 (1970).

(22) J. J. McCullough and C. W. Huang, *Can. J. Chem.*, **47**, 757 (1969).

Column chromatography was done on 0.05–0.2-mm silica gel (E. Merck, Darmstadt) from Brinkmann Instruments, Westbury, N. Y. Analytical precoated tlc plates of silica gel F-254 with fluorescent indicator (E. Merck, Darmstadt) were obtained from Brinkmann Instruments. Unibars were from Analtech, Wilmington, Del.

Vpc work was done on a Hewlett-Packard (F & M Scientific) Research Chromatograph, Model 5750, using a 6 ft  $\times$  0.125 in. column of 10% silicone gum rubber (UC-W98) on Chromosorb G (80–100 mesh, AW-DMCS).

**Photocycloadditions of Carbostyrils with Olefins.**—In general a 0.03–0.18 *M* solution of the carbostyril and 10 equiv of olefin in a suitable solvent (*N,N*-dimethylacetamide or ethanol) was purged with nitrogen and irradiated through quartz in the Srinivasan-Griffin photochemical reactor of the Southern New England Ultraviolet Co. equipped with 3500-Å fluorescent lamps. The irradiation was followed by tlc [10% (v/v) 2-propanol in benzene] and continued until the starting material disappeared (20 hr–2 weeks). The ethanolic irradiation mixtures were filtered to remove the precipitated dimer, and the filtrate was concentrated to dryness on a rotary evaporator. In other solvents the solution was concentrated and the residue was triturated or extracted with ethanol to separate the dimer. The products were purified normally by recrystallization, evaporative distillation, or sublimation. In a few cases, as indicated in the text, the reaction mixtures were separated by column chromatography. All reaction mixtures when analyzed by vpc gave one peak with the retention expected for the adduct unless otherwise specified.

**4,4,5,5-Tetramethyl-3,6-dihydrocyclobuta[c]-2-quinolone (2a).**—Compound 1 (10.0 g) and tetramethylethylene (58 g) in a 700-ml ethanol solution gave 0.94 g of **3** and 14.3 g of **2a**: mp 197–198.5° (from acetone, 63% overall yield); ir (KBr) 1666  $\text{cm}^{-1}$  (amide C=O);  $\nu \lambda_{\text{max}}^{\text{EtOH}}$  259  $\mu\text{m}$  ( $\epsilon$  8600); nmr ( $\text{CDCl}_3$ )  $\delta$  9.48 (brs, 1, NH), 6.98 (m, 4, ArH), 3.26 (q, 2,  $J_{\text{AB}} = 10.4$  Hz, cyclobutane CHCH), and 1.30, 1.19, 1.05, and 0.78 ppm (4 s, 12, 4  $\text{CH}_3$ ).

**5,5-Dimethyl-3,6-dihydrocyclobuta[c]-2-quinolone (2b).**—Compound 1 (1.00 g) and isobutylene (17 g) in a 700-ml ethanol solution gave 4.0 g of **3** and 7.90 g of **2b**: mp 172.5–173.5° (acetone, 39%); ir (KBr) 1668  $\text{cm}^{-1}$  (C=O);  $\nu \lambda_{\text{max}}^{\text{EtOH}}$  259  $\mu\text{m}$  ( $\epsilon$  8830); nmr ( $\text{CDCl}_3$ )  $\delta$  9.59 (brs, 1, NH), 6.95 (m, 4, ArH), 3.45 (m, 2, cyclobutane, CHCH), 2.34 (m, 2, cyclobutane  $\text{CH}_2$ ), and 1.27 and 0.86 ppm (2 s, 6, 2  $\text{CH}_3$ ).

**5,5-Diethyl-3,6-dihydrocyclobuta[c]-2-quinolone (2c).**—Compound 1 (6.0 g) and 2-ethyl-1-butene (34.8 g) in a 700-ml ethanol solution gave 3.0 g of **3** and 4.61 g of **2c**: mp 152–153° (acetone, 35%); ir (KBr) 1663  $\text{cm}^{-1}$  (C=O); nmr ( $\text{CDCl}_3$ )  $\delta$  9.81 (brs, 1, NH), 7.00 (m, 4, ArH), 3.54 (m, 2, cyclobutane, CHCH), 2.28 (m, 2, cyclobutane  $\text{CH}_2$ ), 1.65 (q, 2,  $\text{CH}_2\text{CH}_3$ ), 1.25 (q, 2,  $\text{CH}_2\text{CH}_3$ ), 0.93 (t, 3,  $\text{CH}_3$ ), and 0.60 ppm (t, 3,  $\text{CH}_3$ ).

**5,5-Dimethoxy-3,6-dihydrocyclobuta[c]-2-quinolone (2d).**—Compound 1 (100 mg) and dimethyl ketene acetal<sup>14</sup> (650 mg) in 25 ml of *N,N*-dimethylacetamide gave 170 mg of **2d**: mp 167–168.5° (acetone, 40%); ir (KBr) 1666  $\text{cm}^{-1}$  (C=O); nmr ( $\text{CDCl}_3$ )<sup>23</sup>  $\delta$  9.73 (brs, 1, NH), 7.04 (m, 4, ArH), 3.95 (d, 1,  $J_{\text{AB}} = 9.56$  Hz, cyclobutane CHCH), 3.32, 3.05 (2 s, 6, 2  $\text{OCH}_3$ ), 3.3–2.85 (m, 1, cyclobutane CHCH, hidden under  $\text{OCH}_3$ ), and 2.83–2.50 ppm (d, 2, cyclobutane  $\text{CH}_2$ ).

**5-Methoxy-3,6-dihydrocyclobuta[c]-2-quinolone (2e).**—Compound 1 (10.0 g) and vinyl methyl ether (24.9 g) in a 700-ml ethanol solution gave 3.50 g of **3** and 9.1 g of **2e** (vpc indicated two adducts with  $t_R$  29.7 and 36.2 min,  $T$  160°, in a 2:1 ratio): mp 124–135° (acetone, 33%); ir (KBr) 1661  $\text{cm}^{-1}$  (C=O); nmr ( $\text{CDCl}_3$ )  $\delta$  10.13, 9.92 (2 brs, 2, 2 NH), 7.08 (m, 8, ArH), 3.31, 3.25 (2 s, 6, 2  $\text{OCH}_3$ ), and 4.42–2.0 ppm (brm, 10, cyclobutane CHCH and  $\text{CH}_2$ ). After three recrystallizations, vpc indicated one isomer ( $t_R$  29.7 min): mp 149.5–151° (acetone, 4%); ir (KBr) 1661  $\text{cm}^{-1}$  (C=O); nmr reported in Table V.

(23) The nmr of **2d** was a deceptively simple spectrum; see E. O. Bishop in "Annual Review of NMR Spectroscopy," Vol. 1, E. F. Mooney, Ed., Academic Press, New York, N. Y., 1968, pp 125–127.

**5-Cyano-3,6-dihydrocyclobuta[c]-2-quinolone (2f).**—Compound 1 (7.25 g) and acrylonitrile (27.5 g) in a 700-ml ethanol solution gave 3.7 g of **3** and 6.32 g of **2f** [vpc indicated two adducts with  $t_R$  12.6 min,  $T$  192° (not separated) and tlc indicated a ratio of 1.4:1]: mp 164–176° (ethanol, 42%); ir (KBr) 1666  $\text{cm}^{-1}$  (C=O); nmr ( $\text{DMSO}-d_6$ )  $\delta$  10.20 (brs, 1, NH), 7.17 (m, 4, ArH), and 4.42–2.08 ppm (brm, 5, cyclobutane CHCH and  $\text{CH}_2$ ). Trituration of the original reaction mixture gave 0.95 g (16%) of one isomer (lower  $R_f$ , lower  $t_R$ ) by tlc: shrinks at 215°; mp 229.5–231.5°; ir (KBr) 1666  $\text{cm}^{-1}$  (C=O); nmr ( $\text{DMSO}-d_6$ ) reported in Table VI.

**5-Acetoxy-3,6-dihydrocyclobuta[c]-2-quinolone (2g).**—Compound 1 (10.0 g) and vinyl acetate (60 g) in a 700-ml ethanol solution gave 2.2 g of **3** and 1.32 g of **2g**: mp 190.5–192.0° (acetone, 4.4%); ir (KBr) 1729 (acetyl C=O) and 1669  $\text{cm}^{-1}$  (amide C=O); nmr ( $\text{CDCl}_3$ )  $\delta$  9.75 (brs, 1, NH), 7.08 (m, 4, ArH), 5.06 (m, 1, cyclobutane CHCH), 4.18–2.25 (brm, 4, cyclobutane CHCH and  $\text{CH}_2$ ), and 2.09 ppm (s, 3,  $\text{CH}_3$ ). The yield was low because product mixed with polymerized vinyl acetate was difficult to purify.

**5-*n*-Butoxy-3,6-dihydrocyclobuta[c]-2-quinolone (2h).**—Compound 1 (10.0 g) and vinyl *n*-butyl ether (69 g) in a 700-ml ethanol solution gave 2.0 g of **3** and 13.3 g of **2h**: mp 121.5–122.5° (acetone, 40%); ir (KBr) 1670  $\text{cm}^{-1}$  (C=O); nmr ( $\text{CDCl}_3$ )  $\delta$  9.62 (brs, 1, NH), 7.04 (m, 4, ArH), 4.08 (m, 2, cyclobutane CHCH), 3.60–2.0 (brm, 5, cyclobutane CHCH,  $\text{CH}_2$ , and  $\text{OCH}_2$ ), and 1.75–0.60 ppm (brm, 7,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ).

**4,4,5,5-Tetrachloro-3,6-dihydrocyclobuta[c]-2-quinolone (2i).**—Compound 1 (7.25 g) and tetrachloroethylene (82.9 g) in a 700-ml *N,N'*-dimethylacetamide solution gave 0.36 g of **3**, 1.67 g of unreacted 1, and 11.1 g of **2i**: mp 285.5–287.5° (EtOH, 36%); ir (KBr) 1680  $\text{cm}^{-1}$  (C=O); nmr ( $\text{DMSO}-d_6$ )  $\delta$  3.37 (brs, 1, NH), 7.14 (m, 4, ArH), and 4.54 ppm (q, 2,  $J_{\text{AB}} = 10.7$  Hz) cyclobutane CHCH).

**5,5-Diphenyl-3,6-dihydrocyclobuta[c]-2-quinolone (2j).**—Compound 1 (1.0 g) and 1,1-diphenylethylene (12.4 g) in a 125-ml ethanol solution gave 0.20 g of **3** and 0.45 g of **2j**: mp 191.5–192.5° (column chromatography followed by recrystallization from acetone, 7%); ir (KBr) 1673  $\text{cm}^{-1}$  (C=O); nmr (pyridine- $d_6$ )  $\delta$  8.73 (brs, 1, NH), 7.23 (m, 14, ArH), 4.78 (d, 1,  $J_{\text{AB}} = 9.12$  Hz, cyclobutane CH-CH), and 4.20–2.42 ppm (brm, 3, cyclobutane CHCH and  $\text{CH}_2$ ). The yield was low because the product decomposed either as it formed or on the column.

**3,9-Dihydrobicyclo[3.2.0]heptano[6',7'-c]-2-quinolone (2k).**—Compound 1 (10.0 g) and cyclopentene (47 g) in a 700-ml ethanol solution gave 4.6 g of **3** and 8.0 g of **2k**: mp 161° dec (acetone, 38%); ir (KBr) 1668  $\text{cm}^{-1}$  (C=O);  $\nu \lambda_{\text{max}}^{\text{EtOH}}$  258  $\mu\text{m}$  ( $\epsilon$  8550); nmr ( $\text{CDCl}_3$ )  $\delta$  9.23 (brs, 1, NH), 6.98 (m, 4, ArH), and 3.5–1.0 ppm (brm, 10, cyclobutane CHCH and  $\text{CH}_2$ , aliphatic  $\text{CH}_2$ ).

**3,12-Dihydrobicyclo[6.2.0]decano[9',10'-c]-2-quinolone (2l).**—Compound 1 (10.0 g) and cyclooctene (76 g) in a 700-ml ethanol solution gave 4.3 g of **3** and 8.70 g of **2l**: mp 166° dec (acetone, 22%); ir (KBr) 1667  $\text{cm}^{-1}$  (C=O); nmr ( $\text{CDCl}_3$ )  $\delta$  9.47 (brs, 1, NH), 6.98 (m, 4, ArH), and 3.5–0.83 ppm (brm, 16, cyclobutane CHCH and  $\text{CH}_2$ , aliphatic  $\text{CH}_2$ ).

**Registry No.**—Carbostyril, 493-62-9; **2a**, 19045-10-4; **2b**, 19045-11-5; **2c**, 23667-19-8; **2d**, 23667-20-1; **2e**, 19045-12-6; **2f**, 23667-22-3; **2g**, 23667-23-4; **2h**, 23667-24-5; **2i**, 23667-25-6; **2j**, 23667-26-7; **2k**, 19399-15-6; **2k'**, 23667-28-9; **2l**, 23667-29-0.

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