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Cycloaddition. XVIII. Isomer Distributions in the Photosensitized Addition of 1-Chloropropene to Cyclopentadiene

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cis- and *trans*-1-chloropropene have been added to cyclopentadiene with β-acetonaphthone as a photosensitizer at 30.5 and −24.8°. The relative total amounts of cis and trans photocycloadducts are about the same from *cis*- and *trans*-1-chloropropene, but the composition with respect to individual isomers is different in the two products by amounts outside the experimental error. These differences are smaller than in the similar case of the 1,2-dichloroethylenes and, as in that case, are greater at the lower temperature than at the higher. The observed regioselectivities and relative reactivities of olefins toward excited cyclopentadiene triplet are consistent with direct formation of a triplet biradical, whose time of spin inversion to singlet is appreciably shortened by the presence of chlorine within the biradical.

One of the clearest models of cycloaddition through a biradical intermediate is the reaction initiated by a photosensitizer. Triplet excitation energy is transferred rapidly from the sensitizer to that one of the unsaturated reactants having the lower lying triplet. Attack of this triplet on the second reactant produces a biradical with its electron spins unpaired, longer lived than a singlet biradical. Undergoing extensive intramolecular rotational equilibration, this biradical leads to product distributions characteristically different from those of concerted cycloadditions[2] from excited singlet state participants. Cyclopentadiene, sensitized by aromatic ketones, gives photocycloadducts to 1,2-dichloroethylene,[3,4,7,8] 2-butene,[5,7] and 1,2-dichloro-1,2-difluoroethylene,[6,7] which are mixtures of all seven possible cis-fused 1,2 and bridged 1,4 cycloadducts with extensive loss of configuration.

The comparison of the photocycloadditions of 2-butene and 1,2-dichloroethylene[7] revealed a striking difference. Six of the seven products are classifiable as belonging to the erythro or threo series,[10] this configurative feature being established at the moment of formation of the biradical. (The trans 5,6-disubstituted norbornenes are of ambiguous origin, since they can be formed from both erythro and threo biradicals.) *cis*- and *trans*-2-butene lead to identical ratios of the three erythro products, and to identical ratios of the threo products, although the ratio of total erythro to total threo depends upon the configuration of the starting material. This indicates that the internal rotations of each biradical on which the relative amounts of its products depend have reached statistical equilibrium before the spin inversion which triggers cyclization of the biradical. In the dichloroethylene products, however, although the ratio of total cis products to total trans products is largely independent of the configuration of the starting material, the actual isomer distribution within the threo series and within the erythro series shows large variation between cis and trans dichloroethylenes. The product pattern suggested that the sp^2–sp^3 rotation that equilibrates the relative configurations of the two chlorine atoms was still proceeding rapidly, but that the sp^3–sp^3 rotation about the newly formed bond in the biradical must be proceeding less completely. It has recently been established[9] that this ethane-like rotation approaches equilibration at higher temperatures, so that the dichloroethylene photocycloaddition at 80–100° is comparable in degree of equilibration to the 2-butene cycloaddition at −15°.

In the difference between the cases of 2-butene and of 1,2-dichloroethylene several factors may be involved. Since the steric requirements of the chlorine atom and the methyl group are comparable, it seems likely that the difference is more a matter of rate of spin inversion, converting triplet into singlet biradical (concerted or unconcerted with bond formation) than of the rate of intramolecular rotation in the biradical. Chlorine is not a heavy enough nucleus to cause spectacular effects on rates of spin inversion, but a finite influence of this kind is to be expected and could easily produce the marginal effect observed where ring closure just begins to compete with internal rotation. Other possible differences in the systems being compared include persistence of an exciplex in the formation of the biradical, secondary interaction between chlorine and hydrogen in the biradical, "cogwheel" facilitation of rotation past a methyl group as compared to a chlorine atom, and possible donor–acceptor character in the reaction between cyclopentadiene triplet and dichloroethylene providing a possible bypass to the conservation of spin multiplicity. Since the similarities between the butene and dichloroethylene systems are greater than the differences, the last-named factor cannot be very important. The fact that the product compositions are independent of sensitizer over a considerable range of excitation energy[3] makes competition between cyclopentadiene and a dichloroethylene–diene complex as energy acceptor seem unlikely.

Several of the possible influences mentioned here would depend in their operation on whether the chlorine atom, or the methyl group, were at the radical site or at the site of

Table I
VPC Retention Times for Hydrogenated Photoadducts[a]

Compd[b]	Retention time, min
2	59.2
Dihydro-F′	61.8
3 + **5** + dihydro-F	69.7
Dihydro-G	86.9
Dihydro-E	99.3
4	116.2

[a] 25 ft × 0.125 in. TCEP on Chromosorb P 60/80 mesh column at 90° with 5 cm³/min flow rate. [b] For structures see ref 11.

initial bond formation. It was therefore considered of interest to study the photosensitized cycloaddition of cyclopentadiene and 1-chloropropene. Biradicals in this system would resemble those from 2-butene at one point and those from dichloroethylene at the other. If the degree of stereochemical equilibration depended on the regioorientation of the biradical, it would speak for one of the more unsymmetrically operating of the effects.

Results

The photosensitized cycloaddition of a mixture of *cis*- and *trans*-1-chloropropene to cyclopentadiene was shown to produce the 12 photocycloadducts listed in Scheme I.[11]

The names A Cl or A Me refer to structure A with chlorine and methyl respectively at position 7.

The identification of all the adducts[11] does not complete the problem of determining their relative amounts. It is only from quantitative information that one can evaluate the contributions of the various factors that determine the rate of the biradicals produced in photosensitized reactions. From the separations of the photoadducts on a 25 ft × 0.125 in. column of 20% TCEP on acid-washed Chromosorb P, 60/80 mesh, it was possible to get the relative amounts of fractions $h\nu$1–9 (components listed in Table V of ref 11). On a 30 ft × 0.125 in. TCEP Chromosorb P 80/100 mesh column it proved possible to get the relative amounts of A Cl and A Me, since $h\nu$3 separated sufficiently to give a measurable shoulder. Simultaneous injection of $h\nu$3 and synthetic A Cl indicated that the shorter retention time material was A Cl. The analysis of $h\nu$3 was performed by cutting out the peaks on the chart paper and weighing them. The reproducibility of the analysis for A Cl and A Me proved to be of the order of ±1.0% of the reported value from one injection to the next.

It was therefore possible to get ten numbers by direct analysis of the original photomixture. Many other columns were tried in an effort to get additional separations. The complex nature of the mixture (the cyclopentadiene photodimers overlapped with adducts on many columns) as well as the basic similarity of structures, polarities, and volatilities of the adducts made the effort fruitless.

The key proved to be products of hydrogenation of the photoadduct mixture. The peaks $h\nu$4 and $h\nu$5 each separated into two pure compounds upon hydrogenation. The products of the hydrogenation of $h\nu$4 and $h\nu$5 did not overlap, and hence it was possible, in conjunction with the analysis of the unhydrogenated photomixture, to get a complete analysis of the entire photoadduct mixture. VPC analysis on the 25-ft TCEP column of the mixture obtained by hydrogenating the mixed photoadducts in ethyl acetate over platinum oxide under 1 atm of hydrogen revealed six peaks. Collection, in conjunction with simultaneous injection, indicated the results listed in Table I.

Table II
Product Distribution from Photosensitized Cycloaddition of Cyclopentadiene with *cis*-1-Chloropropene, β-Acetonaphthone as Sensitizer

Compd		30.5°	−24.8°
F	(trans-1,4)	11.8	10.3
C Cl	(erythro, trans-1,2)	7.1	4.8
A Cl	(threo-cis-1,2)	16.9	19.5
A Me	(threo-cis-1,2)	3.4	2.4
B Me	(threo-trans-1,2)	16.2	16.9
G	(exo-cis-1,4)	8.3	10.0
C Me	(erythro-trans-1,2)	12.8	14.2
F′	(trans-1,4)	7.7	8.0
B Cl	(threo-trans-1,2)	11.9	11.2
E	(endo-cis-1,4)	1.5	0.9
D Me	(erythro-cis-1,2)	0.3	0.3
D Cl	(erythro-cis-1,2)	2.1	1.5
Cyclopentadiene photodimers		565.	940.

The hydrogenation was shown to be quantitative by using dodecane as an internal standard. The above results therefore allow for a complete analysis of all 12 components of the photoadduct mixture. The procedure consists of (a) analysis of the isolated photoadducts $h\nu$1–9 on the 25 ft × 0.125 in. TCEP column; (b) analysis of A Cl and A Me on the 30 ft × 0.125 in. TCEP column; (c) hydrogenation of the isolated adduct mixture; (d) analysis of the hydrogenated photoadducts on the 25 ft × 0.125 in. TCEP column.

From d the amounts of hydrogenated G and hydrogenated F′ (dihydro-G and dihydro-F′) are directly measurable. The amount of dihydro-G when subtracted from the amount of $h\nu$4 gives the amount of B Me. The amount of dihydro-F′ when subtracted from the amount of $h\nu$5 gives C Me. Cross checking of the results, for instance, by taking the amount of **2** (obtained from the analysis of hydrogenation products) and subtracting the amount of B Cl ($h\nu$6) to obtain the amount of B Me indicated agreement within a run to about ±0.5–1% of the reported values.

All the quantitative analyses were performed using an F & M 7620 dual-column flame ionization chromatograph with nitrogen as carrier gas. The integrations were performed with an F & M 3370 digital integrator except as previously indicated. The detector was assumed to be equally sensitive to the various isomeric adducts. The products were shown to be stable to the photolytic conditions under which they were formed.

No reproducible quantitative results could be obtained in the case of *cis*-1-chloropropene and cyclopentadiene when irradiated at −78°. The amount of cross adducts from the cis isomer was less than 5% of the amount of photocyclopentadiene dimers.

The results of the photosensitized cycloadditions are given in Tables II and III. The experiments were all performed in degassed, sealed Pyrex tubes containing samples of either *cis*- or *trans*-1-chloropropene, freshly distilled cyclopentadiene, and 2-acetonaphthone in the approximate molar ratio of 100:10:1, respectively. The chloro olefins were of >98% purity.

Discussion

In broad terms, the photosensitized cycloaddition of 1-chloropropene to cyclopentadiene resembles that of 1,2-dichloroethylene[3,7] in yielding nonidentical product distributions from cis and trans starting materials. Also in simi-

Table III
Product Distribution from Photosensitized Cycloaddition of Cyclopentadiene with *trans*-1-Chloropropene, β-Acetonaphthone as Sensitizer

Compd		30.5°	-24.8°	-78.0°
F	(trans-1,4)	16.9	21.0	29.8
C Cl	(erythro, trans-1,2)	11.3	4.8	1.33
A Cl	(threo-cis-1,2)	19.9	21.4	23.2
A Me	(threo-cis-1,2)	4.1	3.1	1.3
B Me	(threo-trans-1,2)	9.1	5.3	3.8
G	(exo-cis-1,4)	4.3	2.4	1.4
C Me	(erythro-trans-1,2)	9.1	7.6	4.6
F′	(trans-1,4)	11.3	23.5	28.8
B Cl	(threo-trans-1,2)	10.7	8.0	3.7
E	(endo-cis-1,4)	1.5	1.4	1.2
D Me	(erythro-cis-1,2)	0.4	0.3	0.1
D Cl	(erythro-cis-1,2)	1.4	1.2	0.8
Cyclopentadiene photodimers		240.	289.	390.

Table IV
Structural and Stereochemical Distribution of Photocycloadducts of Tables II and III

	30.5°		-24.8°	
	From cis	From trans	From cis	From trans
Total cis	30.4	31.6	34.6	28.0
Total 1,2	70.7	66.0	70.8	51.7
Total 1,2 with $\cdot CHCH_3$	32.7	22.7	33.8	16.3
Total 1,2 with $\cdot CHCl$	38.0	43.3	37.0	35.4
Total erythro-1,2	22.3	22.2	20.8	13.9
Total threo-1,2	48.4	43.8	50.0	37.8
trans-1,4 (F + F′)	19.5	28.2	18.3	44.5
endo-cis-1,4 (E)	1.5	1.5	0.9	1.4
exo-cis-1,4 (G)	8.3	4.3	10.0	2.4
Total erythro-1,2 Me	13.1	9.5	14.5	7.9
Total threo-1,2 Me	19.6	13.2	19.3	8.4
Total erythro-1,2 Cl	9.2	12.7	6.3	6.0
Total threo-1,2 Cl	28.8	30.6	30.7	29.4

larity to the case of dichloroethylene, the total *cis/trans ratio* of the products near room temperature shows no significant dependence on the configuration of the starting material. The differences between the products from the cis and trans isomers, which are more marked at the lower temperatures, appear in a greater regioselectivity of the cyclopentadiene triplet toward the trans than the cis isomer, and in the distribution between 1,2- and 1,4-addition products. Thus the generalization that the sp^2–sp^3 rotation in the biradical is fast relative to spin inversion applies to this case also. There is a scattered incidence of cis–trans pairs formed with slight net inversion (PQ < 1),[12,13] but since these instances in the 1,2-addition products are almost exactly balanced by net retentions in the 1,4 products, they are probably associated with fractionations in the ring closing step. Exploring this point in great detail is hindered by the impossibility of determining what fraction of the 1,4 cycloadducts originate from the Me and the Cl biradicals, and how the trans 1,4 adducts are apportioned between erythro and threo series.

The 1,2 cycloadducts, however, are readily recognizable both as to the regio series (Cl or Me) and as to the diastereomeric series (erythro and threo)[10] to which they belong. Table IV summarizes such information about the product distributions at 30.5 and −24.8°. In general the dependence on configuration of starting material is greater than with 2-butene, but less than with 1,2-dichloroethylene.[3,5,7] There is, however, no tendency for the Cl product distribution to resemble specifically those from dichloroethylene, or those from 2-butene; rather, the results are consistent with the idea that the presence of a single chlorine atom in the triplet biradical gives it a lifetime with respect to spin inversion that is intermediate between those of biradicals with two chlorine atoms and with none.

If an intramolecular heavy atom effect is the correct explanation of the difference between the lifetimes of triplet biradicals that do and do not contain chlorine, it is surely a marginal effect. Experiments with two halogen-containing solvents (1,1,2-trichloro-1,2,2-trifluoroethane and bromobenzene) showed no significant effect of the solvent on the product compositions of the cycloadducts of cyclopentadiene with *cis*- and *trans*-2-butene. However, it should be noted that the spin inversion with which we are here concerned is that of an odd electron at one end of a rapidly rotating biradical in which the environment of the electron and its interaction with its mate are constantly changing. In the large heavy atom solvent effects on the dimerization of acenaphthylene,[14] intersystem crossing occurs in the rigid excited singlet of acenaphthylene crossing to triplet *before* the formation of any biradical. Even the time scales of these two cases are quite different so that the lack of solvent effects in the present case probably does not constitute a test of an intramolecular heavy atom effect in a biradical.

Because of the competition for cyclopentadiene triplet by the olefin and ground-state cyclopentadiene, it is possible to evaluate the competitive rate constants from an accurate determination of the relative amounts of reactants and products. The rate constants of reaction of cyclopentadiene triplet with a series of alkenes can thus be determined in terms of its rate constant toward cyclopentadiene as a standard.

In the competing reactions (D = diene, O = olefin, D_2 = dimer, A = adduct, D* = excited diene)

$$D^* + D \xrightarrow{k_d} D_2$$

$$D^* + O \xrightarrow{k_a} A$$

$$-d(D)/dt = 2k_d(D^*)(D) + k_a(D^*)(O)$$

$$-d(O)/dt = k_a(D^*)(O)$$

$$\frac{d(D)}{d(O)} = 2\frac{k_d}{k_a}\frac{(D)}{(O)} + 1 \qquad (1)$$

If (D)/(O) = x and (O) = y, then

$$\frac{dy}{y} = \frac{dx}{\left(2\frac{k_d}{k_a} - 1\right)x + 1} \qquad (2)$$

If k is defined as $2(k_d/k_a) - 1$, the integral equation is

$$\ln\frac{y_0}{y} = \frac{1}{k}\ln\frac{kx_0 + 1}{kx + 1} \qquad (3)$$

which can be applied to the initial and final amounts of material in a preparative reaction. When, as in most of the present cases, irradiation is conducted to the complete consumption of cyclopentadiene, the final x vanishes and the equation becomes

$$\ln\frac{y_0}{y} = \frac{1}{k}\ln(kx_0 + 1) \qquad (4)$$

Table V
Relative Reactivities toward Cyclopentadiene Triplets (Total Cycloadducts)

Alkene, x_0 = 0.10	R^a 30.5°	R^a -24.8°	$10^4\ k_a/k_d$ from eq 4 30.5°	$10^4\ k_a/k_d$ from eq 4 -24.8°	Ref
cis-1-Chloropropene	5.65	9.40	42	22.5	This work
Cl orientation[c]			22.5	11.8	This work
Me orientation[c]			19.5	10.7	This work
trans-1-Chloropropene	2.40	2.89	121	96	This work
Cl orientation			79.4	66	This work
Me orientation			41.6	30	This work
cis-1,2-Dichloroethylene	1.47[b]	2.29	230[b]	128	3
trans-1,2-Dichloroethylene	0.39[b]	0.45	1081[b]	909	3
2-Butene	33[b]		(5[b])		5

[a] R = (cyclopentadiene dimers)/(cross adducts). [b] At 25°. [c] Assuming that the distribution of 1,2 cycloadducts indicates the regioselectivity in formation of the total biradical.

When y is in great excess, the approximation

$$\ln\frac{y_0}{y} \approx \frac{A}{y_0}$$

becomes a good one, and eq 3 becomes equivalent to that previously used[15] in cycloadditions of 1,1-dichloro-2,2-difluoroethylene. By means of eq 4 the relative rate constants of Table V have been determined. A trans olefin captures cyclopentadiene triplet at 30.5° 2.9 times as fast as its cis isomer in the case of 1-chloropropene, and 4.7 times as fast in the case of 1,2-dichloroethylene at 25°. At −24.8° these factors become 4.3 and 7.1, respectively.

The k_a/k_d of 2-butene in Table V is of low accuracy because the dimers were only estimated retrospectively by difference from the initial diene and the measured yield of cross adduct. The value is included for qualitative comparison only.

Comparison of the rates in Table V suggests that at the site of first bond formation methyl is more deactivating than chlorine by factors of about 7 and 5, respectively, in the trans and cis alkenes, while chlorine at the radical site is more activating than methyl by corresponding factors of 13 and 6. The results are consistent with the rate of photosensitized cycloaddition being chiefly determined by local factors stabilizing a free radical and hindering the formation of a covalent bond. There are no signs of these factors being greatly modified by energy uptake by a complex nor by the entrance of an exciplex into the reaction sequence under the conditions of these reactions.

Experimental Section

Materials for Quantitative Photosensitized Cycloadditions. Eastman dicyclopentadiene was cracked thermally to give cyclopentadiene. The cyclopentadiene to be used in a run was redistilled shortly before use. Eastman White Label β-acetonaphthone was recrystallized from hexane. Pure *trans*-1-chloropropene (98+%) was obtained by distillation of practical 1-chloropropene through a 23-in. Nester-Faust spinning band column with a reflux ratio of 50–100:1, bp 37.5–38.0°. Pure *cis*-1-chloropropene (98+%) was obtained by redistillation of the 31–34° fraction from the isolation of trans olefin through the 23-in. Nester-Faust column. Pure cis olefin was obtained at 32.5–33.0° with a reflux ratio of about 100:1. The VPC analysis of these olefin mixtures was performed on either a 15 ft × 0.25 in., 15% tricresyl phosphate on Chromosorb P 60/80 mesh column or a 25 ft × 0.125 in., 20% 1,2,3-tris(cyanoethoxy)propane on acid-washed Chromosorb P 60/80 mesh column.

Irradiations. The olefin (5.0 g, 0.066 mol), freshly distilled cyclopentadiene (0.45 g, 0.0066 mol), and β-acetonaphthone (0.11 g, 0.00066 mol) were weighed into 15 × 125 mm Pyrex test tubes with constricted necks. The tubes were degassed four times and sealed under vacuum. A 550-W Hanovia mercury lamp was used for all irradiations. For the runs at 0° and above the tubes were fastened to a Pyrex well and immersed in a water bath. The water bath was kept at the desired temperature by passing cold methanol from a Lauda Kryomat Model TK30 through cooling coils. Water circulated through the Pyrex well. The runs at −24.8° were performed by placing the sealed tubes in a Pyrex flask containing enough dimethyl ether to cover the tubes. The well containing the lamp was placed next to the flask. The dimethyl ether was refluxed using the well as a heat source and a Dry Ice condenser. A stream of dry nitrogen was blown on the face of the flask adjacent to the lamp to prevent the condensation of moisture. The experiments at −78° were performed by immersing the sealed tubes in a Dry Ice–methanol bath contained in an unsilvered dewar. The Pyrex well containing the lamp was then placed adjacent to the side of the dewar next to which the tubes were suspended.

Product Analysis. An F & M 7620 dual column gas chromatograph with a flame ionization detector was used. The tubes were opened and the olefin was examined for isomerization. In no case was the product olefin analysis different from that of starting olefin within experimental error. The olefin was distilled off and the residue was bulb-to-bulb distilled at 0.001 mm into a liquid nitrogen cooled receiver. The peaks $h\nu$1–9 were analyzed on a 25 ft × 0.125 in. 20% TCEP on Chromosorb P 60/80 mesh column at 90° and 5 cm^3/min He flow rate. The relative amounts of A Cl and A Me were determined on a 30 ft × 0.125 in. 20% TCEP on Chromosorb P 80/100 mesh column at 90° and less than 1 cm^3/min flow rate. To about 0.03 g of this photomixture was added 2 mg of PtO_2 and about 0.5 ml of ethyl acetate. The hydrogenation was carried out under 1 atm of hydrogen for about 4 hr (uptake generally halted after 0.5 hr). The ethyl acetate solution was then decanted (after centrifugation) and analyzed directly in the 25 ft TCEP column for the hydrogenation products of Δ2 and Δ3. All integrations were performed using an F & M 3370 digital integrator except those for the relative amounts of A Cl and A Me. These were obtained by Xeroxing the VPC trace and cutting out the peaks corresponding to A Cl and A Me and weighing them.

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Registry No.—A Cl, 53835-16-8; A Me, 53835-17-9; B Cl, 53861-69-1; B Me, 53861-70-4; C Cl, 53861-71-5; C Me, 53861-72-6; D Cl, 53861-73-7; D Me, 53861-74-8; E, 53835-18-0; F, 53861-75-9; F′, 53861-76-0; G, 53835-19-1; cyclopentadiene, 542-92-7; *cis*-1-chloropropene, 16136-84-8; *trans*-1-chloropropene, 16136-85-9.

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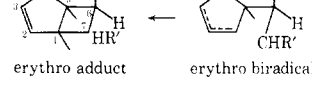
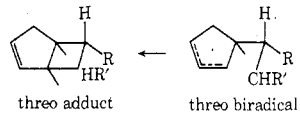


erythro adduct erythro biradical



threo adduct threo biradical

to the front. The erythro, threo designations apply to the relative configurations at C_5 and C_6 in the allylic biradical, which are permanently established when the first bond is formed. The radical ends are regarded as corresponding substituents.

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Synthesis and Solvolytic Studies of Tetracyclo[4.2.0.0^{2,5}.0^{4,7}]octan-3-yl (Secocubane) Derivatives

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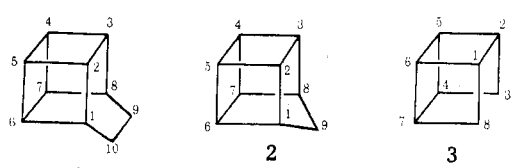
An efficient synthesis of pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one (**5**, homocubanone) has been devised and its conversion to a variety of tetracyclo[4.2.0.0^{2,5}.0^{4,7}]octan-3-yl (secocubane) derivatives is described. Baeyer–Villiger oxidation of *exo*-secocubyl methyl ketone (**14**) gave the corresponding acetate **15**, which was reduced to exo alcohol **16**. Similar oxidation of *endo*-secocubyl methyl ketone (**13**) gave acetate **18** and trifluoroacetate **19**, shown to have the rearranged *exo*-tetracyclo[4.2.0.0^{2,4}.0^{3,8}]octan-5-yl structure. *exo*-Secocubyl mesylate (**17**) solvolyzed in acetic acid with a rate of $k = 1.27 \times 10^{-4}$ sec^{-1} at 75°, and gave one product, acetate **18**. The results obtained in this investigation are compared with the reactivity of *exo*- and *endo*-bicyclo[2.2.0]hex-2-yl derivatives and explained in terms of controlling steric, geometric, and conformational factors.

The study of strained polycyclic small-ring compounds has become widespread in recent years.[1] In particular, the use of the cubane "cage" compound series pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decyl (bishomocubyl), pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}] (homocubyl), and cubane itself has facilitated the study of strain–reactivity relationships. Investigations with derivatives of these cage compounds have given insight into the nature of transition metal catalyzed rearrangements of strained systems,[2] and solvolysis studies of bishomocubyl (**1**)[3] and homocubyl (**2**)[4] derivatives have offered exceptional opportunities for the investigation of transition states, intermediates, and strain release factors in carbonium ion rearrangements.

A natural extension to the studies of cubane-related cage compounds is the tetracyclo[4.2.0.0^{2,5}.0^{4,7}]octyl (secocubane) system (**3**). These solvolytic studies of secocuban-3-yl derivatives (**4**) offer exceptional opportunities for the study of the geometrical and stereochemical requirements of carbonium ion rearrangements in strained systems. The pucker[5,6] of the side cyclobutane rings in the rigid secocubyl cage causes a large stereochemical difference in the rearrangement routes open to the exo and endo isomers of **4**. Furthermore, one would anticipate significant differences in exo vs. endo reactivities in the secocubyl series.



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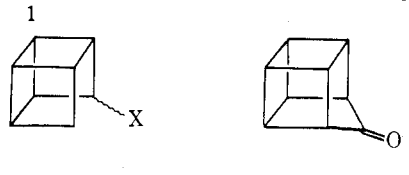

4 5

The discovery of the intramolecular [2 + 2] photocycloaddition reaction has lead to the development of synthetic routes to a variety of polycyclic cage compounds.[7] However, the difficulties which make these compounds such a synthetic challenge often hamper further studies. The multistep, low-yield synthetic routes to homocubanes[8] and secocubanes[9] limit the quantities of material available for solvolytic and other chemical investigations. We now wish to describe the development of a convenient and efficient synthesis of homocubanone (**5**) which makes large quantities of ketone available for use as a synthetic intermediate. We also wish to report, in detail, on the conversion of **5** to monofunctionalized secocuban-3-yl derivatives, and the studies undertaken of the solvolytic reactivity of the secocubane compounds.

Synthesis. The synthesis of homocubanone was accomplished by the series of reactions outlined in Scheme I. The synthesis of tetrachlorohomocubanone ketal **9** was first reported by Warrener and coworkers;[10] however, no experimental details were given and no attempt was made to optimize the yield. In the present study, it has been found that a 65% yield of **6** could be obtained when the reactants were refluxed in *n*-octane (bp 125°) for 6 days.[11,12] Dechlorination of **9** with lithium metal and *tert*-butyl alcohol in tetrahydrofuran[13] gave homocubanone dimethyl ketal (**10**) in 90% yield. Ketal **10** was hydrolyzed to homocubanone (**5**) with 5% aqueous sulfuric acid. The sequence illustrated in Scheme I represents a 30% overall yield synthesis of **5** from cyclooctatetraene, and is capable of providing 20–30-g quantities of material for further synthetic efforts.

Conversion of **5** to the secocubane system was achieved via nonenolizable ketone cleavage.[14] Thus, when **5** was added to a stirred suspension of potassium *tert*-butoxide and water in tetrahydrofuran, and the mixture was heated at 50° for 6 hr, an 85% yield of a mixture of *endo*-and *exo*-secocubane-3-carboxylic acids (**11** and **12**) in a 9:1 ratio was obtained. The NMR spectrum of the mixture of **11** and **12** contained broad singlet resonances at δ 2.3 for **11** and 2.5 for **12** (in a ratio of 9:1) for the methylene protons and a broad multiplet at δ 3.0–3.7 for the remaining cage protons of both isomers. The upfield shift of the methylene protons of endo isomer **11** is consistent with the results found for