Photochemical Cycloadditions of Maleic Anhydride and Some Derivatives to Acenaphthylene. A New Route to Pleiadienes[1]

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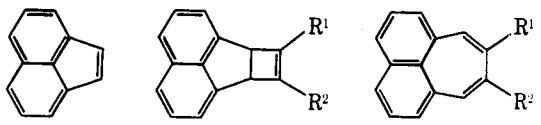
Acenaphthylene (1) reacts photochemically with maleic anhydride and some substituted maleic anhydrides in halogenated solvents to form cyclobutane derivatives **4** and **5**. These photoadducts can be converted to cyclobutene derivatives **2** *via* oxidative bisdecarboxylation. Both dehydrohalogenation of **6c** and **6d** and dehalogenation of **6e** provide a convenient route to cyclobutene **2f**. Thermal isomerization of cyclobutenes, **2a**, **2b**, and **2f**, affords a facile synthesis of pleiadienes **3a**, **3b**, and **3f**.

Pleiadiene (**3a**) and related nonalternant hydrocarbons have long been a subject of theoretical interest.[3] In 1956, the synthesis of the parent compound, pleiadiene, was first reported.[4] However, extremely low yields from lengthy synthetic schemes precluded an investigation of the physical and chemical properties of this substance. We wish now to report a more convenient route to **3a**[5] and some substituted pleiadienes *via* thermal isomerization of various 6b,8a-dihydrocyclobut[*a*]acenaphthylenes (**2**). These cyclobutene derivatives are readily obtained from the photochemically produced cycloadducts of **1**[6] with various substrates.



1 **2** **3**

2,3	a	b	c	d	e	f	g
R^1	H	CH_3	Cl	Br	Cl	CO_2CH_3	CO_2H
R^2	H	H	H	H	Cl	CO_2CH_3	CO_2H

Since the most direct synthesis of compounds **2** appeared to be the photochemical cycloaddition of **1** to alkynes, irradiation of **1** in the presence of acetylene, 2-butyne, hexafluoro-2-butyne, phenylacetylene, diphenylacetylene, and dimethylacetylene dicarboxylate was attempted. Under various conditions of solvent, temperature, and photosensitization, no cycloadducts were obtained; only dimerization[7] of **1** was observed.

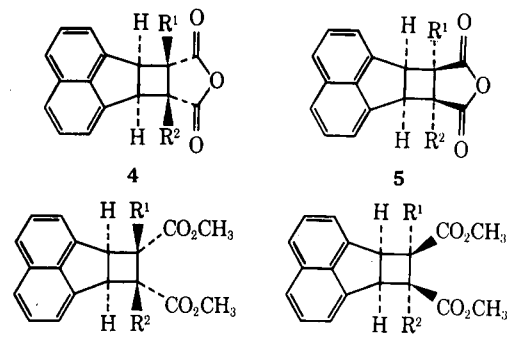
We then turned our attention to the photoaddition of **1** to various olefins, appropriately substituted so as to offer a facile conversion of the cycloadduct to the desired cyclobutene **2**. For this purpose, a series of olefins, which have been widely used to photochemically generate cyclobutane adducts, were chosen. However, irradiation of **1** in the presence of vinyl acetate, vinylene carbonate, vinyl chloride, and other chlorinated ethylenes again afforded only the well-known photodimers of **1**.

In view of the successful photoaddition of maleic anhydride to phenanthrene,[8] it seemed feasible to attempt the synthesis of compounds **2** through cycloaddition of **1** to various maleic anhydride derivatives. An examination of the literature revealed two previous investigations of the attempted addition of maleic anhydride to acenaphthylene (**1**). In 1962, Bryce-Smith[9] observed only polymer formation when a dioxane solution of **1** and maleic anhydride was irradiated. Similar results were obtained in the presence of benzophenone or benzil as sensitizers. Schenck and Wolgast[10] reported that the dimerization was inhibited when **1** and maleic anhydride were irradiated in the presence of Rose Bengal. Since it appeared likely that this inhibition could be caused by the formation of a cycloadduct between **1** and maleic anhydride, we repeated these experiments. We found that, even in the absence of light, the addition of maleic anhydride to solutions of Rose Bengal or similar sensitizers in acetonitrile caused a fading of the dyes.

We then turned our attention to the heavy-atom effect, which had been successfully applied to the photodimerization of **1**[11] and its cycloaddition to acrylonitrile[12] or cyclopentadiene.[13] We found that irradiation of **1** and maleic anhydride in heavy-atom solvents afforded the desired cycloadduct,[14] along with a copolymer and the two dimers of **1**.

Table I illustrates the product distribution in this reaction as a function of solvent. The yield of cycloadduct **4a** increases proportionally with atomic number of the halogen atom in the solvent, at the expense of dimer and copolymer formation. Further experiments indicated that pure heavy-atom solvents were unnecessary; **4a** was readily formed in acetonitrile containing only 10% methyl iodide. Interestingly, in this solvent system small amounts (3%) of the syn isomer **5a** were formed.

The limited solubility of **4a** and **5a** precluded a direct elucidation of their stereochemistry by nmr spectroscopy. However, conversion of these adducts to the corresponding dimethyl esters **6a** and **7a** by reactions in which isomerization is not expected to occur offered a means of establishing their stereochemistry. The methoxy protons in the anti isomer **6a** exhibit a chemical shift of δ 3.76, while the corresponding signal in the syn form **7a** is shifted to higher field (δ 3.2) owing to shielding by the aromatic nucleus (see Table II). Additional confirmation of the stereochemical assignment was obtained by ozonolysis of **6a** and **7a**, oxidative work-up, and conversion of the resulting acids to the known *cis,trans,cis*-[15] and *cis,cis,cis*-1,2,3,4-tetracarbomethoxycyclobutanes,[16] respectively. The identities of the tetraesters were established by spectral and melting point comparisons with authentic samples.



4 **5**

6 **7**

4, 5, 6, 7	a	b	c	d	e
R^1	H	CH_3	Cl	Br	Cl
R^2	H	H	H	H	Cl

Table I
Product Distribution from Irradiation of 1 and Maleic Anhydride as a Function of Solvent

Solvent	Yield,[a] % 1 dimers[b]	Yield,[a] % Copolymer	Yield,[a] % 4a	Conversion of 1, %
Dioxane	97			17
Acetone	61	29		50
Acetonitrile	35	51		53
Dichloromethane	11	25	56	49
Dibromomethane	12	18	70	47
Iodomethane	13		81	47

[a] The yields are based on recovered starting material 1. [b] Trans:cis ratio of dimers varied with solvent.

Encouraged by the results with maleic anhydride, we investigated the photoaddition of several substituted maleic anhydrides to 1. Irradiation of acetone or dioxane solutions of citraconic anhydride and 1 gave only dimers of 1 and traces of polymer. However, when 1,2-dibromoethane was used as solvent, cycloadduct **4b** was formed in 53% yield. The nmr spectrum of **4b** shows a singlet at δ 1.0 (CH_3), a doublet at δ 3.03 (CHCO), a multiplet at δ 4.45 (benzylic protons), and a multiplet at δ 7.55 (aromatic protons) in the ratio of 3:1:2:6. The anti configuration of **4b** was deduced from a comparison of the chemical shifts of the methoxy protons in its dimethyl ester **6b** (δ 3.8 and 3.74) with those of the two ester isomers **6a** and **7a** derived from the maleic anhydride adduct (see Table II). It can be seen that the methoxy protons in anti isomers **6a–e** exhibit lower field absorption than the syn isomers **7a** and **7e**.

Interestingly, attempts to form a cycloadduct between 1 and dimethylmaleic anhydride, under a variety of experimental conditions, were unproductive.

The successes achieved through the use of a heavy-atom solvent in the photoaddition of maleic and citraconic anhydrides to 1 suggested to us the possibility of incorporating a "heavy atom" into one of the addends. Thus, monochloro-, monobromo-, and dichloromaleic anhydrides were irradiated with 1 in both halogenated and nonhalogenated solvents. When solutions of these anhydrides and 1 in acetone, acetonitrile, or cyclohexane were exposed to light, only the dimers of 1 and/or polymeric products were formed. One exception was observed. Small amounts of adducts **4c–e** were isolated when dioxane was employed as solvent. Yields of these cycloadducts were increased (45%) in the presence of such heavy-atom solvents as ethyl bromide or 1,2-dibromoethane. In the case of addition of dichloromaleic anhydride to 1, both the anti isomer **4e** and the syn isomer **5e** were obtained.

Proof of structure and stereochemical assignment of cycloadducts **4c–e** and **5e** were based on the nmr spectral data of the cycloadducts and the dimethyl esters derived from them (see Experimental Section and Table II).

Conversion of cycloadducts 4 to cyclobutene derivatives 2 was accomplished by several methods. Electrolytic decarboxylation has been described[17] as a convenient method for the preparation of small-ring alkenes from vicinal cyclobutanedicarboxylic acids. However, only traces of compounds of the type 2 could be detected in the best cases when the diacids from 4 were subjected to varying experimental conditions, such as different electrolytes and voltages. Somewhat better results were obtained by means of oxidative bisdecarboxylation[18] of either the anhydride adduct or the corresponding diacid. For example, treatment of **4a** with lead tetraacetate in pyridine afforded cyclobutene **2a** in *ca.* 20% yield. Similar treatment of the diacid from **4a** gave *ca.* 30% yield of **2a**. No improvement in yield was noted when the oxidation was carried out in benzene–pyridine or dimethyl sulfoxide.[19] Similarly, anhydrides **4b–e** and the corresponding diacids were converted to cyclobutenes **2b–e** in yields of 10–20%.

Table II
Chemical Shifts[a] (δ) of Methoxy Protons in Esters 6 and 7

	a	b	c	d	e
6	3.76	3.80, 3.74	3.90, 3.75	3.85, 3.72	3.87
7	3.20				3.20

[a] In $CDCl_3$.

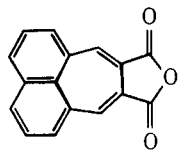
The structures of **2a–e** were established by means of spectral data (see Experimental Section). The structure of **2a** was further confirmed by catalytic hydrogenation to the known 6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene.[20]

While cyclobutenes **2a–e** were formed in only modest amounts, diester **2f** was readily obtained by dehydrohalogenation of **6c** and **6d**. For example, treatment of monochloro ester **6c** with triethylamine in refluxing dioxane afforded a 90% yield of cyclobutene **2f**, which was also obtained by a similar treatment of **6d**. Quantitative yields of **2f** were obtained by treatment of dichloro ester **6e** with nickel tetracarbonyl in benzene in the presence of catalytic amounts of dimethylformamide.[21] The structure of **2f** was proven by catalytic hydrogenation to the syn diester **7a**, also obtained from photoadduct **5a**. Interestingly, **2f** exists in two crystalline modifications, an unstable colorless form, mp 119–121°, and a stable yellow form, mp 131–132.5°. Cyclobutene diacid **2g** was also obtained in good yield by dehydrobromination of either anhydride adduct **4d** or the corresponding bromo diacid. The unsaturated acid **2g** obtained in this way was identical with material prepared by alkaline hydrolysis of diester **2f**.

The ring opening of cyclobutenes 2 was accomplished thermally. The parent compound, pleiadiene (**3a**), was formed in 50% yield when a decalin solution of **2a** was maintained at 200° for 2 hr. A more efficient conversion of **2a** to **3a** was effected by passing a benzene solution of **2a** through a steel tube heated to 480° using steam as a carrier gas. Under these conditions, quantitative yields of **3a** were obtained. The structure of **3a** was verified by comparison of its melting point and ultraviolet–visible spectrum with those reported[4] and also by catalytic hydrogenation to pleiadane.[22] Similarly, thermal isomerization of **2b** gave 8-methylpleiadiene (**3b**) in 90% yield. This novel pleiadiene readily formed a Diels–Alder adduct with maleic anhydride, by analogy to that previously reported for pleiadiene.[4] On the other hand, we were unable to accomplish the analogous ring isomerization of the halogenated cyclobutenes **2c–e**. The formation of the pleiadiene structures **3c–e** was indicated by the usual deep-red color of the thermolysis mixtures; however, only inseparable product mixtures were obtained in these cases. Apparently considerable decomposition,[23] such as dehydrohalogenation, accompanied the ring-opening process.

In contrast, dimethyl 8,9-pleiadienedicarboxylate (**3f**) was formed in 80% yield when a solution of **2f** was heated in refluxing diphenylmethane (265°) for 10 min. Like its precursor **2f**, pleiadiene **3f** exhibits dimorphic behavior. Depending on the recrystallization solvent, two forms of **3f** were obtained, an unstable deep-red form, mp 95–96°, and a stable orange form, mp 110–112°. Although pyrolysis of **2g** afforded pleiadiene diacid **3g**, attempts to purify the crude acid by sublimation or recrystallization from boiling solvents resulted in dehydration to the pleiadiene anhydride **8**. The crude diacid **3g** was converted to diester **3f** on treatment with diazomethane. Catalytic hydrogenation

of **3f** afforded a mixture of *trans*-dimethyl 8,9-pleiadanedicarboxylate[4] and the previously unknown cis isomer **11**. The structure and stereochemical assignment of **11** were established by comparison with material independently prepared by conversion of the trans diacid **9**[4] to anhydride **10**, followed by esterification. Treatment of cis diester **11** with sodium methoxide in refluxing methanol gave exclusively the trans isomer, having physical and spectral properties identical with those reported.[4a]



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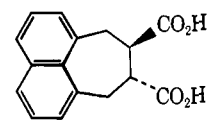

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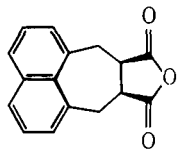

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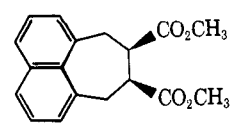

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In conclusion, photocycloaddition of maleic anhydrides to **1** appears to offer a convenient route to the synthesis of pleiadienes. Further extensions of these syntheses, investigation of the physical and chemical properties of pleiadienes, and particularly a study of the mechanism of photoaddition of **1** to maleic anhydride derivatives are presently in progress.

Experimental Section[24]

Attempted Cycloaddition of 1. Solutions of **1** (2 mmol) and 6–12 mmol of diphenylacetylene, dimethyl acetylenedicarboxylate, vinyl acetate, vinyl trifluoroacetate, trichloroethylene, vinylene carbonate, vinyl isobutyl ether, 2-butyne, or hexafluoro-2-butyne in 7 ml of acetone, dioxane, or 1,2-dibromoethane were irradiated under N_2 using a GWCa filter ($\lambda > 330$ nm). After evaporation of the solvent the residue was analyzed by thin layer or vapor phase chromatography. Only dimers of **1** were indicated. Column chromatographic separations of the reaction products afforded 200–250 mg of cis and trans dimers of **1**.

Similarly, only dimers of **1** were obtained when solutions of **1** and the above-mentioned substrates were irradiated in acetone, acetonitrile, benzene, or methanol in the presence of various sensitizers (benzil, benzophenone, Rose Bengal, or erythrosine).

***anti*-6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid Anhydride (4a).** A solution of 8.5 g of **1** and 15.0 g of maleic anhydride in 150 ml of dibromomethane was irradiated for 48 hr. Filtration gave 0.35 g of the trans dimer of **1**. Evaporation of the filtrate left a solid residue, which was triturated with two 75-ml portions of anhydrous ether to dissolve unreacted **1** (4.5 g) and maleic anhydride. The ether-insoluble residue was treated with 150 ml of boiling benzene and filtered to give 1.1 g of insoluble copolymer. Evaporation of the benzene filtrate and fractional crystallization of the residue from benzene or ethyl acetate gave 0.1 g of the cis dimer of **1** and 4.3 g (70%) of **4a**, mp 235–236°, nmr (CD_2Cl_2) δ 7.45–8.0 (m, 6), 4.55 (broad d, 2), 3.40–3.52 (m, 2).

Anal. Calcd for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03. Found: C, 76.50; H, 3.97.

Hydrolysis of 4a. A solution of 40.6 g of **4a** in 400 ml of 1.5 *N* methanolic KOH and 50 ml of water was heated at reflux for 2 hr. The reaction mixture was poured onto ice and acidified with 10% HCl. The precipitate was filtered, dried, and recrystallized from acetone to give a quantitative yield of the diacid of **4a**, mp 223–226°.

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.45; H, 4.55.

Esterification of 4a. A solution of 3.0 g of **4a** in 80 ml of methanol was treated with 0.5 ml of concentrated H_2SO_4 and heated at reflux for 4 hr. The solution was evaporated to one-half its volume, poured onto 100 ml of water, and extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated to give, after recrystallization from chloroform–ether, 3.1 g (87%) of **6a**, mp 153°, nmr ($CDCl_3$) δ 7.25–7.78 (m, 6), 4.52 (m, 2), 3.76 (s, 6), 3.27 (m, 2).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.90; H, 5.45.

Ozonolysis of 6a. Ozone was bubbled at a rate of 1.65 g/hr through a suspension of 1.3 g of **6a** in 150 ml of acetic acid for 16 hr at 20°. The resulting clear solution was heated at reflux for 8 hr with 12 ml of 30% hydrogen peroxide and subsequently treated with an additional 20 ml of H_2O_2 and allowed to stand at room temperature for 48 hr. The solution was evaporated at 0.5 mm and the residue was treated with an ethereal solution of diazomethane until a yellow color persisted. Evaporation of the solvent and recrystallization of the residue from benzene gave 0.56 g (44%) of *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane, mp 144–145° (lit.[15] mp 145°).

***syn*-6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid Anhydride (5a).** Irradiation of a solution of 10.0 g of **1** and 15.0 g of maleic anhydride in 114 g (90 mol %) of acetonitrile and 43.7 g (10 mol %) of methyl iodide for 17 hr afforded precipitation of 1.75 g of the trans dimer of **1**. The filtrate was evaporated at 12 mm and the residue was treated with 100 ml of diethyl ether and 30 ml of petroleum ether. Filtration of the insoluble material and recrystallization from benzene gave 3.2 g (39%) of **4a**. Evaporation of the mother liquor, subsequent fractional crystallization from ethyl acetate, and vacuum sublimation gave 0.3 g (4%) of **5a**, mp 264° (crystal modification at *ca.* 230°), nmr (pyridine-d_5) δ 7.33–7.86 (m, 6), 4.60–4.86 (m, 2), 4.15–4.40 (m, 2).

Anal. Calcd for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03. Found: C, 76.70; H, 4.09.

Further evaporation of the mother liquors gave 5.0 g of unreacted **1** and 1.1 g of the cis dimer of **1**.

Hydrolysis of 5a. The diacid of **5a**, obtained by the procedure described for **4a**, was recrystallized from dioxane–hexane, mp 233–234° dec.

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.70; H, 4.27.

Dimethyl Ester of 5a. The diacid from **5a** was treated in the usual manner with ethereal diazomethane to give dimethyl ester **7a**, recrystallized from ethyl acetate–petroleum ether, mp 157–158°, nmr ($CDCl_3$) δ 7.32–7.76 (m, 6), 4.39–4.63 (m, 2), 3.88–4.12 (m, 2), 3.20 (s, 6).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.00; H, 5.49.

Ozonolysis of 7a. Treatment of 1.3 g of **7a** with ozone as described above for **6a** afforded 0.2 (18%) of *cis,cis,cis*-1,2,3,4-tetracarbomethoxycyclobutane, mp 212–213° (lit.[16] mp 203–204°).

7-Methyl-*anti*-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid Anhydride (4b). Irradiation of a solution of 10.0 g of **1** and 15.0 g of citraconic anhydride in 160 ml of 1,2-dibromoethane led to precipitation of 1.9 g of the trans dimer of **1**. Evaporation of the filtrate and recrystallization of the residual solid from ethyl acetate gave 4.1 g (39%) of **4b**, mp 168°. Column chromatography of the mother liquor on silica gel, with ethyl acetate as eluent, afforded 3.8 g of unreacted **1**, 0.7 g of the cis dimer of **1**, and an additional 1.5 g (14%) of **4b**, nmr ($CDCl_3$) δ 7.25–7.87 (m, 6), 4.23–4.64 (m, 2), 2.94–3.02 (broad d, 1), 0.99 (s, 3).

Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.00; H, 4.64.

Hydrolysis of 4b. As described above, the diacid was prepared from anhydride **4b** and recrystallized from dioxane–ether, mp 234–236°.

Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.20; H, 5.04.

Dimethyl Ester of 4b. Treatment of the diacid of **4b** with diazomethane gave dimethyl ester **6b** as colorless crystals (from ether–petroleum ether), mp 85°, nmr ($CDCl_3$) δ 7.21–7.90 (m, 6), 4.39–4.75 (m, 2), 3.80 (s, 3), 3.74 (s, 3), 2.59–2.90 (m, 1), 1.15 (s, 3).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.60; H, 5.63.

7-Chloro-*anti*-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid Anhydride (4c). A solution of 10.0 g of **1** and 17.5 g of freshly distilled chloromaleic anhydride in 160 ml of 1,2-dibromoethane was irradiated for 48 hr. The solvent was evaporated *in vacuo* and the residue was treated with 150 ml of absolute ether. Filtration of the insoluble material and recrystallization from ethyl acetate gave 0.8 g of the trans dimer of **1** and 13.6 g (66%) of adduct **4c**, mp 214–215°, nmr (DMSO-d_6) δ 7.29–7.98 (m, 6), 4.23–4.82 (m, 2), 3.18 (d, 1).

Anal. Calcd for $C_{16}H_9ClO_3$: C, 67.50; H, 3.19; Cl, 12.45. Found: C, 67.50; H, 3.13; Cl, 12.50.

Further concentration of the mother liquors gave 0.5 g of unreacted **1**.

Hydrolysis of 4c. The diacid from **4c**, obtained in the usual manner, was recrystallized from acetone, mp 251–254° dec.

Anal. Calcd for $C_{16}H_{11}ClO_4$: C, 63.47; H, 3.64; Cl, 11.73. Found: C, 63.40; H, 3.66; Cl, 11.50.

Dimethyl Ester of 4c. Treatment of the diacid of **4c** with diazomethane gave dimethyl ester **6c** as colorless crystals, mp 115° (from ether–petroleum ether), nmr ($CDCl_3$) δ 7.25–7.84 (m, 6), 4.32–4.82 (m, 3), 3.90 (s, 3), 3.75 (s, 3), 3.28 (d, 1).

Anal. Calcd for $C_{18}H_{15}ClO_4$: C, 65.36; H, 4.57; Cl, 10.72. Found: C, 65.00; H, 4.73; Cl, 10.90.

7-Bromo-*anti*-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid Anhydride (4d). A solution of 6.0 g of **1** and 7.0 g of bromomaleic anhydride in 130 ml of ethyl bromide after irradiation for 10 hr precipitated 7.4 g (50%) of **4d**, mp 216–217° (recrystallized from acetone–hexane), nmr (DMSO-d_6) δ 7.35–8.00 (m, 6), 4.20–4.87 (m, 2), 3.25 (d, 1).

Anal. Calcd for $C_{16}H_9BrO_3$: C, 58.38; H, 2.75; Br, 24.27. Found: C, 58.34; H, 2.61; Br, 24.57.

Hydrolysis of 4d. The diacid of **4d**, obtained in the usual manner, was recrystallized from acetone, mp 248–249° dec.

Anal. Calcd for $C_{16}H_{11}BrO_4$: C, 55.36; H, 3.19; Br, 23.02. Found: C, 55.62; H, 3.27; Br 22.48.

Dimethyl Ester of 4d. Diazomethane treatment of the diacid from **4d** gave **6d.** Recrystallization from diethyl ether gave **6d** as colorless needles, mp 108–109°, nmr ($CDCl_3$) δ 7.20–7.90 (m, 6), 4.40–4.90 (m, 3), 3.29 (s, 3), 3.79 (s, 3), 3.47 (d, 1).

Anal. Calcd for $C_{18}H_{15}BrO_4$: C, 57.62; H, 4.03; Br, 21.30. Found: C, 57.63; H, 3.97; Br, 21.35.

7,8-Dichloro-*anti*-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid Anhydride (4e). Irradiation of a solution of 10.0 g of **1** and 20.0 g of dichloromaleic anhydride in 160 ml of 1,2-dibromoethane for 48 hr afforded, after filtration and recrystallization from ethyl acetate, 9.1 g (72%) of adduct **4e**, mp 244–245°, nmr (CD_3NO_2) δ 7.46–8.00 (m, 6), 4.98 (s, 2).

Anal. Calcd for $C_{16}H_8Cl_2O_3$: C, 60.22; H, 2.52; Cl, 22.22. Found: C, 60.10; H, 2.36; Cl, 22.10.

Hydrolysis of 4e. Diacid from **4e**, obtained in the usual manner, was recrystallized from benzene–hexane, mp 227–229° dec.

Anal. Calcd for $C_{16}H_{10}Cl_2O_4$: C, 56.99; H, 2.97; Cl, 21.07. Found: C, 57.30; H, 2.97; Cl, 20.80.

Dimethyl Ester of 4e. The usual treatment of hydrolyzed **4e** with diazomethane gave diester **6e**, recrystallized as colorless crystals from ethyl acetate–petroleum ether, mp 158°, nmr ($CDCl_3$) δ 7.23–7.88 (m, 6), 4.94 (s, 2), 3.87 (s, 6).

Anal. Calcd for $C_{18}H_{14}Cl_2O_4$: C, 59.19; H, 3.86; Cl, 19.41. Found: C, 59.10; H, 3.83; Cl, 19.50.

7,8-Dichloro-*syn*-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid Anhydride (5e). After separation of the anti isomer **4e** from the irradiation mixture (above), the resulting filtrate was evaporated and the residue was dissolved in ethyl acetate. Chromatography on a silica gel column with ethyl acetate as eluent afforded 4.0 g of unreacted **1**, 0.6 g of the trans dimer of **1**, 0.1 g of the cis dimer of **1**, an additional 0.6 g (5%) of **4e**, and 0.4 g (3%) of syn adduct **5e.** Recrystallization from ethyl acetate–petroleum ether gave an analytical sample of **5e**, mp 214°, nmr ($CDCl_3$) δ 7.42–7.95 (m, 6), 4.92 (s, 2).

Anal. Calcd for $C_{16}H_8Cl_2O_3$: C, 60.22: H, 2.52; Cl, 22.22. Found: C, 60.20; H, 2.60; Cl, 22.20.

Hydrolysis of 5e. The diacid, obtained in the usual manner, was recrystallized from acetone–water, mp 205–206° dec.

Anal. Calcd for $C_{16}H_{10}Cl_2O_4$: C, 56.99; H, 2.97; Cl, 21.07. Found: C, 57.00; H, 2.92; Cl, 21.00.

Dimethyl Ester of 5e. Diazomethane treatment of the diacid of **5e** afforded dimethyl ester **7e**, mp 139–140° (recrystallized from ether–petroleum ether), nmr ($CDCl_3$) δ 7.33–7.80 (m, 6), 4.78 (s, 2), 3.20 (s, 6).

Anal. Calcd for $C_{18}H_{14}Cl_2O_4$: C, 59.19; H, 3.86; Cl, 19.41. Found: C, 59.10; H, 3.80; Cl, 19.60.

6b,8a-Dihydrocyclobut[*a*]acenaphthylene (2a). A. A solution of 12.5 g (0.05 mol) of **4a** in 180 ml of dry pyridine was treated with 30.0 g (*ca.* 0.07 mol) of lead tetraacetate while maintaining the temperature between 50 and 60° with stirring and exclusion of air. When carbon dioxide evolution (760 ml) had ceased, the temperature was raised to between 70 and 80° and maintained at that temperature for 1 hr. The solvent was evaporated *in vacuo* and the residue was stirred for 2 hr with 500 ml of benzene and 200 ml of 5% aqueous HCl. The benzene phase was separated, washed with water until neutral, dried over sodium sulfate, and evaporated. The residue (6.0 g) was chromatographed with *n*-hexane on a silica gel column to give, after recrystallization from hexane, 1.64 g (18%) of crystalline **2a**: mp 117–119° (lit.[14] mp 118–119°); uv λ_{max} (EtOH) 320 nm (ε 1100), 315 (1300), 306 (4900), 301 (5550), 293 (8200), 290 (sh, 7600), 281 (6800), 272 (sh, 4300), 227 (60,000); nmr ($CDCl_3$) δ 7.00–7.72 (m, 6), 6.24 (s, 2), 4.54 (2, s). The spectral data for **2a** was identical with those reported.[14]

Anal. Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.25; H, 5.67.

B. To a solution of 32.2 g (0.12 mol) of the diacid from **4a** (described above) in 100 ml of pyridine was added 90.0 g (0.2 mol) of lead tetraacetate in portions at 30°. The reaction mixture was slowly warmed to 60–70° and within 30 min 3100 ml of carbon dioxide had evolved. After stirring at 80° for an additional 2 hr, the reaction mixture was cooled in ice and treated with 300 ml of benzene and 300 ml of 10% HCl. The organic phase was separated and poured onto a silica gel column to give 5.9 g (29%) of **2a.**

6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylene. A solution of 210 mg of **2a** in 20 ml of methyl acetate was hydrogenated in the presence of 20 mg of 5% Pd/C at 20° at atmospheric pressure. Filtration of the catalyst and evaporation of the solvent gave, after recrystallization from *n*-hexane, the dihydro compound, mp 79.5–80.5° (lit.[20] mp 78–78.5°). The nmr spectrum of this compound was identical with the published spectrum.

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.10; H, 6.90.

7-Methyl-6b,8a-dihydrocyclobut[*a*]acenaphthylene (2b). A solution of 26.4 g (0.1 mol) of **4b,** 1.4 ml of water, and 100 ml of pyridine was heated at 120° with stirring under dry nitrogen for 10 min. After cooling to 30°, 70.0 g (0.15 mol) of lead tetraacetate and 150 ml of pyridine were added. The reaction mixture was gradually warmed; gas evolution began at 50°; and, while the temperature was maintained at 70°, 2750 ml of carbon dioxide was collected. Work-up, as described above for **2a,** gave 3.2 g (17%) of **2b** as a light yellow oil. Molecular distillation gave **2b,** bp 150–160° (0.7 mm), nmr ($CDCl_3$) δ 7.04–7.73 (m, 6), 6.01 (m, 1), 4.50 (broad s, 2), 1.70 (m, 3).

Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.50; H, 6.31.

7-Chloro-6b,8a-dihydrocyclobut[*a*]acenaphthylene (2c). Treatment of 14.3 g (0.05 mol) of **4c** in 50 ml of dry pyridine and 50 ml of dry benzene with 30.0 g (*ca.* 0.07 mol) of lead tetraacetate at 70° resulted in the evolution of 775 ml of carbon dioxide. The usual work-up, followed by filtration over silica gel, gave 1.2 g of **2c** as a colorless oil. Molecular distillation of the oil afforded 0.8 g of pure **2c,** bp 121–125° (0.6 mm), nmr ($CDCl_3$) δ 7.05–7.80 (m, 6), 6.10 (d, 1), 4.76 (d, 1), 4.46 (d, 1).

Anal. Calcd for $C_{14}H_9Cl$: C, 79.06; H, 4.26; Cl, 16.67. Found: C, 78.80; H, 4.20; Cl, 17.00.

7-Bromo-6b,8a-dihydrocyclobut[*a*]acenaphthylene (2d). A solution of 33.0 g (0.1 mol) of **4d** in 300 ml of benzene and 200 ml of pyridine was obtained by warming under nitrogen with stirring. Lead tetraacetate (60.0 g, 0.14 mol) was added in portions at 60° and the mixture was brought to 80°. The solution became bright yellow, but only a small amoung of gas evolution was observed. The reaction mixture was then heated at reflux for 2 hr, treated with 100 ml of benzene, and poured onto a 9:1 ice–HCl mixture. Extraction with benzene, followed by the usual work-up, gave a solid residue. Recrystallization from hexane gave 2.2 g (8.5%) of **2d,** mp 56–57°, nmr ($CDCl_3$) δ 7.20–8.00 (m, 6), 6.39 (d, 1), 4.83 (d, 1), 4.59 (d, 1).

Anal. Calcd for $C_{14}H_9Br$: C, 65.41; H, 3.50; Br, 31.08. Found: C, 65.25; H, 3.58; Br, 31.30.

7,8-Dichloro-6b,8a-dihydrocyclobut[*a*]acenaphthylene (2e). Decarboxylation of 16.0 g (0.05 mol) of **4e** in 50 ml of dry benzene and 50 ml of dry pyridine with 30.0 g (0.07 mol) of lead tetraacetate at 60–70° resulted in the evolution of 1250 ml of carbon dioxide. The usual work-up gave 1.7 g (14%) of **2e,** mp 133–134° after recrystallization from *n*-hexane, nmr ($CDCl_3$) δ 7.20–7.77 (m, 6), 4.67 (s, 2).

Anal. Calcd for $C_{14}H_8Cl_2$: C, 68.05; H, 3.26; Cl, 28.69. Found: C, 67.85; H, 3.27; Cl, 28.50.

6b,8a-Dihydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid Dimethyl Ester (2f). A. A solution of 51.2 g (0.155 mol) of **6c** and 23.0 g (0.23 mol) of triethylamine in 500 ml of dry dioxane was heated at reflux for 7 hr. Filtration of the resulting suspension gave 18.7 g (88%) of triethylammonium chloride and, after evaporation of the filtrate, 46.6 g of a tan powder. Two recrystallizations from methanol afforded 40.9 g (90%) of **2f** as yellow, crystalline material, mp 131–132.5°. Colorless crystals of **2f,** mp 119–120°, were obtained when recrystallizations were made from ether–*n*-hexane.

The two crystalline forms of **2f** exhibited identical uv and ir spectra in solution and were thermally interconvertible.

B. A solution of 11.0 g of **6e** in 100 ml of 3:1 benzene-dimethylformamide was heated at reflux with 20 ml of nickel tetracarbonyl for 3 hr. After cooling, the solution was poured onto ice and the aqueous phase was extracted with benzene. The usual work-up gave 9.1 g (100%) of **2f**. An analytical sample was obtained by recrystallization from methanol or ether-*n*-hexane: uv λ_{max} (MeOH) 320 nm (ϵ 1900), 306 (1950), 290 (4900), 280 (5850), 270 (5500), 246 (6300), 223 (82,000); nmr ($CDCl_3$) δ 7.40-7.80 (m, 6), 4.78 (s, 2), 3.77 (s, 6).

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.50; H, 4.81.

Hydrogenation of 2f. A mixture of 500 mg of **2f** and 100 mg of Pd/C in 10 ml of methyl acetate was treated with hydrogen at atmospheric pressure. Filtration of the catalyst and passage of the filtrate over a silica gel column gave, after evaporation of the solvent, quantitative yield of **7a**, mp 154-156°. The melting point of a mixture of **7a** and the material prepared by esterification of **5a** (see above) was undepressed.

6b,8a-Dihydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Acid (2g). A. A solution of 10.0 g of anhydride adduct **4d** and 4.0 g of triethylamine in 150 ml of THF was heated at reflux for 2 hr. The reaction mixture was acidified with 6 *N* HCl and extracted with ether. The ether extract was neutralized, dried, and evaporated and the residue was recrystallized from acetonitrile to give 5.5 g (68%) of **2g** as yellow plates, mp 254-256° dec.

B. A solution of 10.0 g of bromo acid (from hydrolysis of **4d**) and 50.0 g of triethylamine in 250 ml of THF was heated at reflux for 8 hr and worked up as described above to give 6.5 g (72%) of yellow crystalline **2g**, mp 256-257° dec.

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 72.03; H, 3.96.

Pleiadiene (Cyclohepta[*d,e*]naphthalene) (3a). A solution of 11.0 g of **2a** in 110 ml of benzene was dropped through a steel tube (25 × 2 cm) heated to 480 ± 5° by means of an internal flow of steam (1 l./hr). The pyrolysis was carried out over 1.5 hr. The distillate was extracted with *n*-hexane and dried over magnesium sulfate. Evaporation of the solvent gave 11.0 g of red crystalline solid which by nmr analysis consisted of 95% of **3a** and 5% of unreacted **2a**. The mixture was again subjected to pyrolysis (as above) to give 10.9 g of a single product, which upon recrystallization from *n*-pentane gave 9.8 g (89%) of pure **3a**, mp 91-92.5° (lit.[4] mp 87-90°), nmr ($CDCl_3$) δ 6.45-7.30 (m, 6), 5.75-6.20 (m, 2), 5.10-5.50 (m, 2).

Anal. Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.40; H, 5.63.

8-Methylpleiadiene (8-Methylcyclohepta[*d,e*]naphthalene) (3b). A solution of 3.0 g of **2b** in 50 ml of decalin in a Pyrex tube was degassed by successive freezing and evacuation at 10^{-2} mm. The tube was sealed and heated at 200 ± 5° for 4 hr. The resulting deep red solution was chromatographed on silica gel with *n*-hexane as eluent to give 3.0 g of **3b**. An analytical sample was obtained by molecular distillation [bp 180° (0.7 mm)] and melted at 27-30°: uv λ_{max} (EtOH) 548 nm (ϵ 90), 508 (240), 476 (390), 446 (460), 419 (450), 384 (sh, 3300), 372 (6600), 365 (sh, 7100), 356 (8300), 342 (9100), 332 (sh, 6600), 294 (4750), 282 (4950), 276 (sh, 4300), 248 (47,500), 229 (23,000); nmr ($CDCl_3$) δ 6.30-7.50 (m, 6), 5.65-6.10 (m, 2), 5.00-5.35 (m, 1), 1.60 (d, 3).

Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.80; H, 6.17.

Maleic Anhydride Adduct of 3b. A solution of 300 mg of **3b** and 225 mg of maleic anhydride in 15 ml of dry dioxane was heated at reflux for 4 hr. Evaporation of the solvent and recrystallization of the residue from benzene-hexane afforded 190 mg (42%) of Diels-Alder adduct as colorless crystals, mp 203-205°.

Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.60; H, 4.85. Found: C, 78.50; H, 4.92.

Dimethyl 8,9-Pleiadienedicarboxylate (3f). A solution of 5.0 g of **2f** in 50 ml of diphenylmethane was heated at reflux for 10 min and the resulting red solution was chromatographed on a silica gel column. Elution with hexane-benzene gave 4.8 g of red oil. Crystallization from methanol gave 4.0 g (80%) of **3f** as red needles, mp 95-96°. An orange, crystalline form of **3f**, mp 110-112°, was obtained when an ether-hexane solvent system was used for recrystallization: uv λ_{max} (CH_3OH) 425 nm (ϵ 625), 356 (10,000), 333 (sh, 7500), 303 (5300), 250 (44,150), 243 (44,500); nmr ($CDCl_3$) δ 6.75-7.50 (m, 8), 3.72 (s, 6). The two forms of **3f** exhibited identical uv and ir spectra in solution and were thermally interconvertible.

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.60; H, 4.85.

8,9-Pleiadienedicarboxylic Acid Anhydride (8). A solution of 1.0 g of **2g** in 12 ml of diphenylmethane became deep red-brown after heating at reflux for 1.5 hr. Trituration with hexane and filtration gave 1.0 g of brown solid which was recrystallized from acetonitrile to give 0.5 g (50%) of **8** as brown, felted needles, mp 301-302° dec.

Anal. Calcd for $C_{16}H_8O_3$: C, 77.42; H, 3.25. Found: C, 77.56; H, 3.55.

A sample of **8** was hydrolyzed to pleiadiene diacid in refluxing aqueous KOH solution to give crude orange diacid **3g** (shown by ir analysis to contain COOH). Sublimation or recrystallization of **3g** led to dehydration and reformation of anhydride **8**.

Hydrogenation of 3f. Addition of hydrogen at 20° and normal pressure to a mixture of 9.0 g of **3f** and 0.9 g of PtO_2 in 25 ml of methyl acetate, after the usual work-up, gave 9.1 g of a colorless oil. Vapor phase chromatography (Wilkens Aerograph 1520 with a 2 m × 0.6 cm column of 4% polyphenyl ether on Chromosorb GAW-DMCS, programmed at 3°/min) indicated the presence of *trans*- and *cis*-7,8,9,10-tetrahydrocyclohepta[*d,e*]naphthalene-8,9-dicarboxylic acid dimethyl ester in a ratio of 4:1.

Hydrogenation of 3a. A solution of 150 mg of pleiadiene (**3a**) in 30 ml of ethanol was hydrogenated in the presence of 10 mg of PtO_2. Filtration and evaporation of the solvent gave 145 mg of pleiadane as colorless crystals, mp 57-58° (lit.[22] mp 55.5-57°).

7,8,9,10-Tetrahydrocyclohepta[*d,e*]naphthalene-8,9-dicarboxylic Acid Anhydride (10). A solution of 10.8 g of 7,8,9,10-tetrahydrocyclohepta[*d,e*]naphthalene-*trans*-8,9-dicarboxylic acid (**9**) and 9.8 g of anhydrous sodium acetate in 200 ml of acetic anhydride was heated under reflux for 5 hr. The solvent was evaporated at 10 mm and the solid residue was extracted with three 100-ml portions of dry benzene. Evaporation and recrystallization of the residue from chloroform gave 7.5 g (75%) of crystalline **10**, mp 212-213°, nmr ($CDCl_2$) δ 7.24-7.83 (m, 6), 5.45-5.87 (m, 6).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.00; H, 4.83.

7,8,9,10-Tetrahydrocyclohepta[*d,e*]naphthalene-*cis*-8,9-dicarboxylic Acid Dimethyl Ester (11). A solution of 1.1 g of **10** and 2 drops of concentrated sulfuric acid in 50 ml of methanol was heated at reflux for 7 hr; 150 ml of water was added; and the reaction mixture was extracted with five 50-ml portions of ether. The ether extracts were dried and evaporated to give a crystalline residue, which was treated with an ethereal solution of diazomethane until a yellow color persisted. Evaporation of the solvent and recrystallization of the residue from ether-petroleum ether gave 1.0 g (77%) of diester **11**, mp 93-95°, nmr ($CDCl_3$) δ 7.06-7.72 (m, 6), 3.04-4.13 (m, 6), 3.65 (s, 6).

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.45; H, 6.12.

Registry No. 1, 208-96-8; **2a,** 30736-79-9; **2b,** 49686-43-3; **2c,** 49686-44-4; **2d,** 49686-45-5; **2e,** 49686-46-6; **2f,** 32141-41-6; **2g,** 49686-48-8; **3a,** 208-20-8; **3b,** 49686-49-9; **3b** maleic anhydride adduct, 49686-50-2; **3f,** 32141-42-7; **4a,** 32506-83-5; **4a** diacid, 49686-52-4; **4b,** 49839-88-5; **4b** diacid, 49686-53-5; **4c,** 49686-54-6; **4c** diacid, 49636-65-9; **4d,** 49686-66-0; **4d** diacid, 49686-67-1; **4e,** 49686-68-2; **4e** diacid, 49686-69-3; **5a,** 49686-70-6; **5a** diacid, 49686-71-7; **5e,** 49686-72-8; **5e** diacid, 49686-73-9; **6a,** 49686-74-0; **6b,** 49686-75-1; **6c,** 49686-76-2; **6d,** 49686-77-3; **6e,** 49686-78-4; **7a,** 49839-90-9; **7e,** 49686-79-5; **8,** 49686-80-8; **9,** 49686-81-9; **10,** 49686-82-0; **11,** 49686-83-1; maleic anhydride, 108-31-6; citraconic anhydride, 616-02-4; chloromaleic anhydride, 96-02-6; bromomaleic anhydride, 5926-51-2; dichloromaleic anhydride, 1122-17-4; 6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene, 32624-91-2.

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Acenaphthylene was recrystallized from petroleum ether (bp 60–80°). Maleic anhydride and dichloromaleic anhydride were recrystallized from chloroform and ligroin (bp 80–100°). Chloro- and methylmaleic anhydride were fractionally distilled, crystallized at −40° from ether–petroleum ether, and again distilled. All solvents were distilled prior to use.

Photochlorination of Alcohols

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Three limiting conditions have been found for the photochlorination of 1-pentanol. In 70% H_2SO_4, chlorination is the exclusive reaction. Polar effects lead to mild selectivity for remote attack. In 20–40% H_2SO_4 and in CCl_4, oxidation and chlorination compete, but conditions can be chosen to make chlorination >90%. In aqueous acetate buffer, chlorination can predominate over oxidation though both compete. There is good selectivity for δ-chlorination, and the chlorination proceeds *via* the alkyl hypochlorite. Photochlorination of cyclopentanol at pH 5 forms 5-chloropentanal quantitatively.

In the many reviews that cover photochlorination by Cl_2,[2-7] data on alcohols are conspicuously absent. The situation is summarized by Poutsma:[8] "alcohols react rapidly with chlorine by a series of steps which ultimately lead to oxidation and formation of carbonyl compounds and chlorinated carbonyl compounds and radical chlorination is not a generally useful route to chloro alcohols." Reports on photochlorination of ethanol[9] and 1-propanol[10] supported this view.

It was conceived that primary and secondary alcohols might be successfully photochlorinated if the hydroxy group were protected by protonation. Kollonitsch and coworkers[11] had already shown that Cl_2 photochlorinations in H_2SO_4 were successful, and they photochlorinated amino acids and peptides in this way. Since alcohols are half-protonated in ~50% H_2SO_4[12-15] and are converted to hydrogen sulfates in 96% H_2SO_4,[16] an intermediate 70% H_2SO_4 was chosen to give extensive protonation without hydrogen sulfate formation.

1-Pentanol is quantitatively photochlorinated in 70% H_2SO_4 with no detectable oxidation (Table I). Products were converted to acetates for both gc analysis and material balance distillation. For the gc analyses, conversion was limited to 50% by using 0.5 mol of Cl_2/mol of 1-pentanol. For the material balance studies, it was more convenient to use equimolar Cl_2 and 1-pentanol. The distilled products consisted of 1-pentyl acetate, monochloro-1-pentyl acetates, and material characterized as dichloro-1-pentyl acetates from the boiling point. The recovery was 87% of theoretical. The gc bands were identified by exact superposition on bands of authentic samples.

The pattern of the chlorination is typical for alkane chains containing a terminal electronegative substituent. These have been extensively investigated and show avoidance of the α position, partial avoidance of the β position, and near-random attack at the γ position and more remote methylenes.[2-7]

The results with 2-hexanol are similar (Table II) and show that the method is equally successful with secondary alcohols. However, the method may be limited to those alcohols which are small enough to be soluble in 70% H_2SO_4, yet are large enough to have γ and more remote hydrogens. The products from such alcohols typically separate on dilution and this facilitates their isolation.

This accomplished the initial objective and the study could have been terminated at this point. However, we were curious about photochlorination of alcohols in less acidic conditions such as CCl_4, dilute H_2SO_4, and aqueous acetate buffers. The results were unexpected.

These latter results will be better understood if the facts regarding the dark ionic oxidation are presented first. In an air atmosphere and in an aqueous media from acetate buffers at pH 5 to 40% H_2SO_4, Cl_2 rapidly oxidizes 1-pentanol to pentyl pentanoate. Analysis by gc of ether-extractable products showed pentyl pentanoate as the only product and specifically pentanal and pentanoic acid were not detected by gc or by nmr of aqueous Na_2CO_3 extracts. The reaction is complete in several