readily isolated pure simply by extracting them from an aqueous solution into dichloromethane. The starting materials (1) remain completely in the aqueous phase. In this manner, *N*-(*tert*-butyloxycarbonyl)-*O*-methyl-L-serine (**2a**) was obtained as an oil in 45–55% yield from *N*-(*tert*-butyloxycarbonyl)-L-serine (**1a**) using sodium methoxide, and crystalline *N*-*tert*-butyloxycarbonyl)-*O*-methyl-L-threonine (**2b**) was obtained from *N*-(*tert*-butyloxycarbonyl)-L-threonine (**1b**) in 52% yield using sodium isopropoxide. Starting material is recoverable in 30–40% yields. The products contained no detectible amounts of starting material or N-methylated products (amino acid analysis, thin-layer chromatography, NMR), and they were shown to be stereochemically pure (<0.1% D isomer) by conversion to the C-terminal lysyl dipeptides followed by analysis for the diastereomeric dipeptides.[10] The corresponding *N*-benzyloxycarbonyl derivatives could not be obtained readily by the same procedure due to partial decomposition of starting materials and/or lack of selectivity.

Experimental Section

N-(*tert*-butyloxycarbonyl)-L-serine and -L-threonine were purchased from Chemical Dynamics Corp., Plainfield, N.J. The course of the methylations was monitored by 60-MHz ^{1}H NMR spectroscopy in $CDCl_3$ making use of the intensities of the following peaks (δ in ppm relative to Me_4Si): $OC(CH_3)_3$, 1.5; NCH_3, 2.9; OCH_3, 3.4.

***N*-(*tert*-Butyloxycarbonyl)-*O*-methyl-L-serine (2a).** *N*-(*tert*-butyloxycarbonyl)-L-serine (**1a**; 2.05 g, 10 mmol) was dissolved in 100 mL of tetrahydrofuran (distilled over $LiAlH_4$). To this was added 40 mL of sodium methoxide solution (freshly prepared by mixing 2 g of a 50% NaH dispersion in oil (40 mmol), 6 mL of methanol, and 74 mL of THF), and the mixture was shaken for 1 h. Methyl iodide (1 mL) in 10 mL of THF was added, and the mixture was shaken for 1 h. The remainder of the $NaOCH_3$ solution and 2 mL of CH_3I in 10 mL of THF were added, and the mixture was shaken for 18 h. The solvent was removed with a rotary evaporator, the residue was dissolved in 50 mL of water, and the solution was washed with ether and acidified at 0 °C with solid citric acid. The mixture was extracted with ethyl acetate, and the extract was washed with dilute aqueous $Na_2S_2O_3$ and saturated salt solution, dried (Na_2SO_4), and concentrated to an oil. The oil contains *N*-(*tert*-butyloxycarbonyl)-*O*-methyl-L-serine and *N*-(*tert*-butyloxycarbonyl)-L-serine in a 3:2 ratio. The mixture was dissolved in water (30 mL), and the desired product was taken out by extracting it into dichloromethane (1 × 30 mL). Evaporation of the dried solvent gave 1.17 g (55%) of *N*-(*tert*-butyloxycarbonyl)-*O*-methyl-L-serine as an oil, which gave a dicyclohexylammonium salt, crystallized from ethyl acetate–petroleum ether, with mp 115–117 °C and $[\alpha]_D^{23}$ +17.5° (*c* 2.0, methanol).

Anal. Calcd for $C_{21}H_{40}N_2O_5$: C, 63.00; H, 10.07; N, 7.00. Found: C, 62.90; H, 10.20; N, 6.89.

The remaining aqueous phase was saturated with NaCl and extracted with ethyl acetate. Evaporation of the solvent gave 0.68 g (30%) of a mixture containing *N*-(*tert*-butyloxycarbonyl)-L-serine and *N*-(*tert*-butyloxycarbonyl)-*O*-methyl-L-serine in a 5:1 ratio.

The results described above were obtained by carrying out all operations preceding the workup at 5 °C. The same results (45–50% yields) were obtained at 23 °C, or when using powdered $NaOCH_3$ in THF or powdered $NaOCH_3$ in THF (100 mL) containing 2% methanol as the methoxide solution.

***N*-(*tert*-Butyloxycarbonyl)-*O*-methyl-L-threonine (2b).** To a solution of sodium isopropoxide, prepared by mixing 0.40 g of an NaH dispersion in oil (8 mmol) and 2 mL of 2-propanol in 20 mL of purified THF, was added *N*-(*tert*-butyloxycarbonyl)-L-threonine (**1b**) (0.44 g, 2 mmol) and CH_3I (1 mL). The mixture was shaken at 5 °C for 20 h. Workup as described for the isolation of **2a** gave, after crystallization from $CHCl_3$, 0.24 g (52%) of *N*-(*tert*-butyloxycarbonyl)-*O*-methyl-L-threonine: mp 125–127 °C; $[\alpha]_D^{23}$ +7.0° (*c* 2.0, methanol), +2.6° (*c* 2.0, *N*,*N*-dimethylformamide) (lit.[4] oil). A 200-mg (40%) amount of *N*-(*tert*-butyloxycarbonyl)-L-threonine was recovered.

Anal. Calcd for $C_{10}H_{19}NO_5$: C, 51.49; H, 8.21; N, 6.01. Found: C, 51.38; H, 8.28; N, 5.94.

Optical Purities. **2a** and **2b** were coupled with the L and DL isomers of benzyl *N*$^{\alpha}$-(benzyloxycarbonyl)lysinate, and after removal of the protecting groups by catalytic hydrogenation separation of the diastereomeric dipeptides was performed on a 0.9 × 15 cm column of Aminex A-5 resin with a Beckman Model 120B amino acid analyzer using 0.35 N sodium citrate, pH 5.50, as eluting buffer.[10] The elution times (min) were as follows: L-Ser(Me)-L-Lys, 39; L-Ser(Me)-D-Lys, 45; L-Thr(Me)-L-Lys, 38; L-Thr(Me)-D-Lys, 45. The L–D isomers are the enantiomers of the D–L isomers. **2a** and **2b** contained less than 0.1% of the D isomer.

Note Added in Proof: The oily *N*-(*tert*-butyloxycarbonyl)-*O*-methyl-L-serine (**2a**) gradually crystallized after standing at −5 °C for several months. It can be recrystallized readily from chloroform–petroleum ether with the help of seed crystals and has mp 63–65 °C and $[\alpha]^{23}_D$ +6.8° (*c* 1.0, methanol).

Registry No.—**1a**, 3262-72-4; **1b**, 2592-18-9; **2a**, 51293-47-1; **2a** dicyclohexylammonium salt, 69912-63-6; **2b**, 48068-25-3.

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Photocyclization Reactions in Primary Amines. Convenient Synthesis of 1,4-Dihydrophenanthrene

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Photocyclization reactions have been widely investigated, and the synthetic and mechanistic aspects of this type of photoreaction have been amply reported.[1] For example, the photooxidative cyclization of stilbenes to phenanthrenes is a reaction of remarkable generality and synthetic utility for the preparation of various condensed aromatic hydrocarbons.[2] Although the chemical and physical aspects of the interactions of aromatic hydrocarbons with primary, secondary, and tertiary amines have been extensively studied and discussed,[3] the first study into the interactions between an amine (e.g., pyrrole, *N*-methylpyrrole) and an excited singlet stilbene molecule (which undergoes photocyclization) was reported by Kubota and Sakurai as recently as 1972.[4] More recently still, Lewis and Ho investigated the interactions between singlet *trans*-stilbene and several secondary and tertiary alkylamines in polar and nonpolar solvents.[5] In all cases it was shown that the photolytic reactions resulted in addition of the amine to the olefenic bond rather than cyclization.

Primary amines are known to be inefficient quenchers of arene fluorescent states, in contrast to secondary and tertiary amines with which even exciplex formation can be observed.[6] However the exact role of such compounds in the type of reactions under discussion here has not yet been studied in detail. We first reported[7] the reductive photocyclization of 2,3-diphenylbenzo[*b*]furan in primary amine solution, and recently Lapouyade and co-workers[8] observed that primary amines and diamines are efficient catalysts in the nonoxidative photocyclization reactions of several 1,1-diarylethylenes.

We wish to report here the photochemical behavior of *trans*-stilbene (**1a**) and various derivatives (**1b–d**) in propyl-

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Table I. Chemical Yield of Products by Irradiation of 1a–d in Propylamine

	% yield					
	2	3	4	5	6	1
1a	<5	70	5	12	8	<5
1b	<5	75	5	10	5	5
1c	5	60	10	15	5	5
1d	10	50	10	15	<5	10

amine. This reaction proves to be a facile synthetic route to 1,4-dihydrophenanthrenes, compounds which are normally difficult to obtain by the usual preparative methods.

Results and Discussion

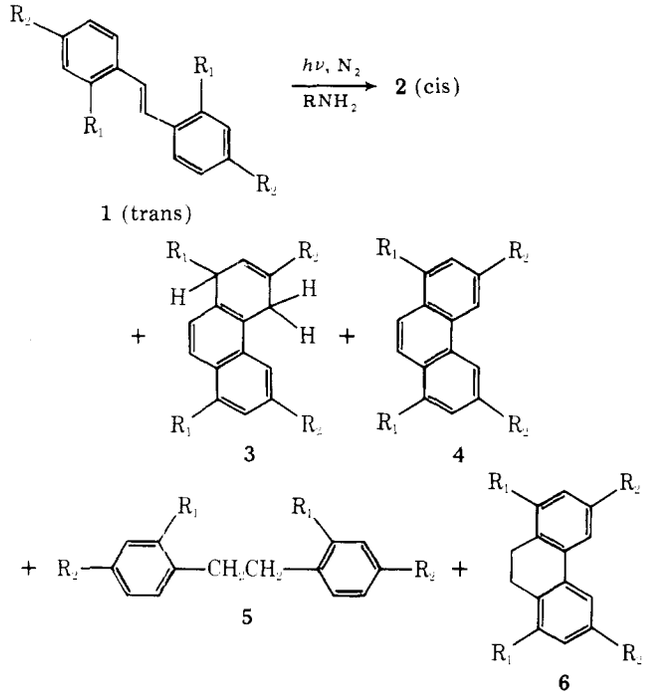
Irradiation at 254 nm of nitrogen-purged propylamine solutions (10^{-2} M) of stilbenes **1a–d** contained in quartz cells gave mainly 1,4-dihydrophenanthrenes **3a–d** (Scheme I). The yields of reaction products (**2–6**) are reported in Table I.

The photoreaction can be performed at higher concentrations (up to 5×10^{-2} M) without considerable changes in the yields, particularly for **3a–d.**

When irradiations were carried out at 313 nm, the same compounds were also obtained, but the chemical yields were relatively lower, particularly for **3a–d** (67, 70, 55, and 47%, respectively) and **6a–d** (5% or less). The quantum yields of formation of **3a,b,d** were estimated at 313 nm: $\Phi_{3a} = 0.085$; $\Phi_{3b} = 0.090$; $\Phi_{3d} = 0.079$.

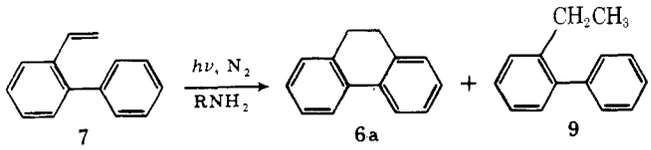
Compounds **3a–d** were readily isolated by chromatographic treatment of the crude photoreaction product on neutral alumina pretreated with silver nitrate (see Experimental Section). Compounds **2** and **4–6** were separated by GLC and identified by comparison of their spectral properties with those of authentic samples prepared from alternative unambiguous reaction sequences. For example, cis analogues **2b–d** of the starting materials and phenanthrene derivatives **4b–d** were obtained using the standard conditions for photoisomerization and photocyclization reactions, respectively, as described by Blackburn and Timmons.[1] Products **5b–d** and **6b–d** were easily obtained by reduction of **1b–d** and **4b–d** with suitable reagents.

Scheme I



a, $R_1 = R_2 = H$; b, $R_1 = H$, $R_2 = CH_3$; c, $R_1 = H$, $R_2 = CH_3O$; d, $R_1 = CH_3$, $R_2 = H$

Scheme II



ratio 9:1

The structures of compounds **3a–d** were inferred by their chemical behavior and confirmed by analysis of spectroscopic data. For example, **3a** did not react with a common dienophile (e.g., *N*-phenylmaleimide[9]) and was thermally dehydrogenated (1) at ~210 °C and (2) at a lower temperature by *p*-chloroanil in toluene solution to yield phenanthrene. The UV spectrum exhibited an absorption (λ_{max}) at 228 nm. The IR spectrum displayed structurally significant absorption bands at 3040 (=CH stretch), 1640 (C=C stretch), 1420 (HC=CH in-plane deformation), and 700 (HC=CH out-of-plane deformation) cm^{-1}. The ^1H NMR signals arising from the two sets of methylene protons were superimposed at δ 3.4. The complexities of the resulting multiplet arise from long-range 1,4-transannular couplings[10] between the methylene protons and also from coupling between these and the neighboring olefinic protons.

Compound **3a** and analogues were evidently absent from the products of Birch reduction of phenanthrenes[11] except for a 9,10-disubstituted derivative.[12] The formation of a compound of which the NMR spectrum was consistent with structure **3a** was reported recently by Richards and coworkers[13] after hydrolysis of the radical anion of phenanthrene. However the 1,4-dihydro derivatives were obtained only as minor products with yields often less than 7%.

The mechanism of the photoformation of the 1,4-dihydrophenanthrene derivatives **3a–d** has not been established. For several reasons preliminary formation of phenanthrene molecules followed by photoreduction by the amine can be excluded; phenanthrenes are readily photoreduced by tertiary amines[14] at the 9,10 positions in accord with theoretical prediction.[15] 9,10-Dihydrophenanthrenes are not key intermediates in the formation of the 1,4 isomers since the amine does not catalyze any thermal or photochemical rearrangement of 9,10- into 1,4-dihydro derivatives. Furthermore, it seems unlikely that the first step of the photoreaction would be the result of an interaction between the primary amine and a phenyl ring of *trans*-stilbenes since primary aliphatic amines should undergo photoaddition of the NH bond at 1,2, 1,3, and 1,4 positions.[16] Subsequent photocyclization of the adduct would not lead to the formation of **3a–d.**

Moreover, it seems that the reductive photocyclization of stilbenes **1a–d** does not correlate with the basicity of the amines since irradiation of **1a–d** in diaminoalkanes (which are known to have higher basicities[17] than primary amines) does not considerably enhance the formation of **3a–d.**

This unusual type of reductive photocyclization seems to be rather limited to 1,2-diarylethylenes. For example, photolysis of 2-vinylbiphenyl in a primary amine does not induce the formation of new unexpected compounds (Scheme II).

Compound **6a** is the predominating photocyclization product,[18] whereas **9** results most probably from the photoreduction of the olefin bond. Interestingly, no trace of **3a** could be detected among the photoreaction products of **7** in the primary amine.

The formation, in good yields, of 1,4-dihydrophenanthrene derivatives by irradiation in a primary amine of stilbene analogues is a general reaction. Such reactions occur not only for 2,3-diphenylbenzo[*b*]furan, as already described,[7] but also for 1,2-diphenylethylene and 2,3-diphenylbenzo[*b*]thiophene.[19]

Experimental Section

General. UV spectra were measured on a Jobin Yvon spectrophotometer. NMR spectra were determined on a Jeol C 60 H instrument with $CDCl_3$ as solvent and tetramethylsilane as internal standard. Mass spectra were recorded on an Riber 10-10 spectrometer. For accurate mass determination, the samples were analyzed on a Mat 311 apparatus. For column chromatography, neutral alumina (Merck Al_2O_3 90, 70–230 mesh) was used with pentane as eluant. Separation and quantitative analyses of the reaction products were effected by GLC. For analytical purposes a 2.1-m column with 100–120 mesh Chromosorb Q support coated with SE 30 was employed. Isolation of the reaction components was achieved using a Varian Autoprep equipped with a 3-m column with Chromosorb W, 100–120 mesh, support coated with OV 101.

Elemental analyses were performed at the CNRS microanalysis center.

The solvents were purified by distillation; the amines were refluxed over potassium hydroxide and distilled immediately before use.

The following abreviations are employed: (s) singlet, (d) doublet, (t) triplet, and (m) multiplet.

Photolyses. Photolyses were carried out in water-cooled quartz reactors equipped with dry nitrogen inlets and magnetic stirrers. Solutions containing *trans*-stilbene or its methoxy or methyl derivatives were purged by bubbling nitrogen through them for 2 h and subsequently irradiated with eight Rul 3000- or 2537-Å lamps (as noted in the text) in a Rayonet RPR photochemical reactor.

The solvents were removed under vacuum, and the crude photreaction product was treated by column chromatograph and/or by GLC.

Quantum Yield Determinations. The measurements were made in a merry-go-round apparatus with an optical bench equipped with a medium-pressure Thorn 250-W mercury lamp. The 313-nm wavelength was selected by using an aqueous solution of potassium chromate (0.2 g L^{-1}) and potassium carbonate (10 g L^{-1}).

The amounts of 1,4-dihydro isomers were measured from VPC after 5–11% conversion. The light intensity was measured by using ferrioxalate actinometry in the modification described by Demas.[38]

Starting Materials. *trans*-Stilbene (**1a**) and *p,p'*-dimethoxy-*trans*-stilbene (**1c**) were purchased (Aldrich Co.) and were recrystallized from 95% ethanol for **1a** (mp 123 °C) and from benzene for **1c** (mp 212 °C).

p,p'- and *o,o'*-dimethyl-*trans*-stilbene were prepared according to the method of Shriner and Berger[20] by reduction of the corresponding benzoin with zinc amalgam. *p,p'*- and *o,o'*-dimethylbenzoin were synthetized by benzoin condensation of *p*- and *o*-tolualdehyde, respectively, in the presence of potassium cyanide.[21] The products were shown to have the trans configuration expected according to the method of synthesis by the presence of intense absorption bands in the 958–967-cm^{-1} region[22] in the respective IR spectra.

***p,p*-Dimethyl-*trans*-stilbene (1b).** This compound was recrystallized from ethanol: mp 179–180 °C (lit.[23] 180 °C); NMR ($CDCl_3$) δ 2.25 (6 H, s), 7.2 (10 H, m, arom.); UV (hexane) λ_{max} 295, 310 nm.

***o,o'*-Dimethyl-*trans*-stilbene (1d).** Condensation of *o*-tolualdehyde and reduction with zinc amalgam of the benzoin afforded **1d**, mp 83–84 °C, after recrystallization from ethanol (lit.[24] mp 83 °C): NMR ($CDCl_3$) δ 2.24 (6 H, s, CH_3), 7 (10 H, m, arom.); UV (hexane) λ_{max} 286 nm.

2-Vinylbiphenyl (7). This compound was prepared by a modified method of Bradsher and Wert.[25] The alcohol obtained by reaction of the Grignard reagent of 2-iodobiphenyl[26] and acetaldehyde was dehydrated by refluxing a solution of the alcohol in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid with simultaneous removal of the azeotrope. The yield was quantitative. **7** was obtained as a colorless oil after distillation [bp 125 °C (5 mm)]: NMR ($CDCl_3$) δ 5.05 (q, J_{AX} = 12 Hz, J_{AB} = 1.5 Hz, 1 H, A part of ABX spectra), 5.55 (q, J_{BX} = 18 Hz, J_{AB} = 1.5 Hz, 1 H, B part), 6.6 (dd, 1 H, X), 7.3 (m, 9 H, arom.); UV (EtOH) λ_{max} 232 nm (ϵ 21 000), 253 (15 500).

Photoconversion of *trans*-Stilbenes to *cis*-Stilbenes. Cis analogues of compounds **1a–c** were obtained by irradiation of a degassed hexane solution of **1a–c** (10^{-2} M) with Rul 3000-Å lamps in a Rayonet reactor for 6 h. GLC analysis clearly showed that the products were predominantly *cis*-stilbenes. Column chromatography of the crude product on alumina using pentane as eluant afforded cis compounds invariably eluted before the trans isomers. *cis*-Stilbene (**2a**) was purchased (Aldrich).

***p,p'*-Dimethyl-*cis*-stilbene (2b).** Irradiation of 210 mg of *trans*-**1b** in 100 mL of degassed hexane yielded 150 mg (70%) of its cis analogue, mp 34–35 °C (lit.[27] 33.8 °C), after recrystallization in hexane: NMR ($CDCl_3$) δ 2.31 (6 H, s, CH_3), 6.41 (2 H, s, olefinic), 6.95 (8 H, m, arom.).

***p,p'*-Dimethoxy-*cis*-stilbene (2c).** From 220 mg of **1c**, irradiated in 100 mL of degassed cyclohexane, 145 mg (65%) of *cis*-**2c** was obtained: mp 34–35 °C (lit.[28] 35 °C); NMR ($CDCl_3$) δ 3.65 (6 H, s, OMe), 6.35 (2 H, s, olefin), 6.85 (8 H, m, arom.); UV ($CHCl_3$) λ_{max} 296 nm.

***o,o'*-Dimethyl-*cis*-stibene (2d).** Irradiation of **1d** (210 mg) and separation as described above afforded **2d**[29] (110 mg, 49%): NMR ($CDCl_3$) δ 2.28 (6 H, s, CH_3), 6.73 (2 H, s, vinyl), 7 (8 H, m, arom.).

Photoconversion of Stilbenes to Phenanthrenes. The general procedure used for the photoconversion of stilbenes to the corresponding phenanthrenes was as follows. A mixture of 10^{-2} M stilbene and 10^{-3} M iodine was dissolved in cyclohexane and irradiated under stirring with Rul 2537-Å lamps in a Rayonet reactor for 12 h. After the solvent was removed, the crude products were chromatographed on alumina using petroleum ether as eluant. The first fractions yielded a mixture of cis and trans isomers. The phenanthrene derivatives were eluted at a later stage and recrystallized from ethanol.

3,5-Dimethylphenanthrene (4b). Irradiation of **1b** (210 mg) in cyclohexane (100 mL) with iodine (26 mg) yielded **4b** (170 mg, 81%): mp 140–141 °C (lit.[30] 141 °C); NMR[31] ($CDCl_3$) δ 2.49 (6 H, s, CH_3), 7.3 (8 H, m, arom.); mass spectrum, *m/e* 206 (M^+, 100).

3,6-Dimethoxyphenanthrene (4c). After irradiation of **1c** (240 mg) in cyclohexane and purification by chromatography on alumina, 190 mg (79%) was obtained: mp 104–105 °C (lit.[32] 104–105 °C); NMR ($CDCl_3$) δ 4.01 (6 H, s, methoxy), 7.5 (8 H, m, arom.); mass spectrum, *m/e* 238 (M^+, 100).

1,8-Dimethylphenanthrene (4d). The low yield for the formation of **4d** is probably due to the presence of two methyl groups in the ortho positions in **1d**. Thus, irradiation of **1d** (210 mg) afforded only 100 mg (45%) of **4d**: mp 188–190 °C (lit.[33] 189 °C); NMR[31] ($CDCl_3$) δ 2.75 (6 H, s, CH_3), 7.35–8 (8 H, m, arom.); mass spectrum, *m/e* 206 (M^+, 100).

1,2-Diarylethanes. Compounds **5a–d** were readily obtained by catalytic reduction of the stilbenes **1a–d** in methanol with activated Pd and hydrogen in the usual manner. The yields were never less than 80%. Compounds **5b**,[23] **5c**,[34] and **5d**[35] were recrystallized from methanol.

9,10-Dihydrophenanthrenes. Compounds **6a–d** were synthesized by hydrolysis of the radical anions of the parent phenanthrenes prepared as described above. The radical anions were generated with lithium metal according to the method of Richards and co-workers.[13] The 9,10-dihydrophenanthrenes were separated by preparative GLC and recrystallized from ethanol. In this way, compounds **6b**,[36] **6c**,[37] and **6d**[38] were produced.

Photolysis of 1a–d in Primary Amines. Solutions of compounds **1a–d** (10^{-2} M) in propylamine were irradiated with Rul 2537-Å lamps for 8 h. The reaction mixtures were evaporated to dryness at reduced pressure in a rotatory evaporator. The photoreaction products were initially purified by elution chromatography on a neutral alumina column in order to remove tarry materials. The relative amounts of the various components were evaluated by subsequent NMR and GLC analyses and comparison with authentic samples.

The procedure for isolation of the 1,4-dihydrophenanthrenes **3a–d** was as follows. The crude photoreaction mixture obtained as described above was dissolved in benzene and poured onto a column of alumina activated with silver nitrate. The chromatography was accomplished in the dark, and the column was eluted with additional petroleum ether. The first fractions contained compounds **5a–d** and **6a–d** followed by **2a–**, **4a–d**, and remaining **1a–d**. The 1,4-dihydro compounds were obtained pure in the following fractions and were recrystallized from pentane at 0 °C.

Final purification of the photoreaction products was achieved by preparative GLC. They were prepared in quantities sufficient for separation and for subsequent NMR analysis. Wherever possible the isolated products were recrystallized. As a further check, retention times were compared with those for authentic samples.

1,4-Dihydrophenanthrene (3a): mp 71–72 °C; NMR ($CDCl_3$) δ 3.3–3.85 (4 H, m, methylene), 5.9 (2 H, m, olefin), 7.2–7.9 (6 H, m, arom.); IR (inter alia) 3040, 2950, 2920, 2860, 2820, 1640, 1600, 1420, 1395, 855, 700 cm^{-1}; mass spectrum, *m/e* 180 (M^+, 100), 178 (62), 165 (37). Precise mass determination: calcd for $C_{14}H_{12}$ 180.093895; found 180.0937. Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 92.29; H, 6.78.

1,4-Dihydro-3,6-dimethylphenanthrene (3b): mp 106–108 °C; NMR ($CDCl_3$) δ 1.86 (3 H, broad s, CH_3), 2.47 (3 H, s, CH_3), 3.45 (4 H, m, CH_2), 5.6 (1 H, m, olefin), 7–7.7 (5 H, m, arom.); mass spectrum, *m/e* 208 (M^+, 100), 206 (65). Precise mass determination: calcd for $C_{16}H_{16}$ 208.125194; found 208.1251. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.76.

1,4-Dihydro-3,6-dimethoxyphenanthrene (3c): mp 84.5–86 °C; NMR ($CDCl_3$) δ 3.5 (3 H, s, OCH_3), 3.57 (4 H, m, CH_2), 3.8 (3 H, s,

OCH_3), 4.8 (1 H, m, olefin), 7.2–8 (5 H, m, arom.); mass spectrum, *m/e* 240 (M^+, 100), 238 (35). Precise mass determination: calcd for $C_{16}H_{18}O$ 240.115022; found 240.1150. Anal. Calcd for $C_{16}H_{18}O$: C, 79.97; H, 6.71; O, 13.32. Found: C, 79.59; H, 6.70; O, 13.63.

1,4-Dihydro-1,8-dimethylphenanthrene (3d): mp 33–34 °C; NMR ($CDCl_3$) δ 1.38 (3 H, m, CH_3), 2.65 (3 H, m, CH_3), 3.65 (3 H, m, CH_2), 5.9 (2 H, m, olefin), 7.5 (5 H, m, arom.); mass spectrum *m/e* 208 (M^+, 100), 206 (70). Precise mass determination: calcd for $C_{16}H_{16}$ 208.125194; found 208.1251. Anal. Calcd for $C_{16}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.32; H, 7.68.

Photolysis of 2-Vinylbiphenyl (7). A solution of compound **7** (10^{-2} M) in propylamine was purged with nitrogen and irradiated with Rul 3000-Å lamps for 8 h. After the amine was removed under reduced pressure, the crude photoreaction product was analyzed by NMR and purified by column chromatography on alumina.

From 180 mg of **7**, 125 mg of **6a** (70%) and 15 mg of **9** (8%) were obtained. The structures of these compounds were established by comparison with authentic samples.

2-Ethylbiphenyl (**9**) was prepared by reduction of the starting material in the usual manner.

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Registry No.—**1a,** 103-30-0; **1b,** 18869-29-9; **1c,** 15638-14-9; **1d,** 36888-18-3; **2a,** 645-49-8; **2b,** 2510-76-1; **2c,** 2510-75-0; **2d,** 20657-42-5; **3a,** 20244-28-4; **3b,** 69795-78-4; **3c,** 69795-79-5; **3d,** 69795-80-8; **4a,** 85-01-8; **4b,** 1576-67-6; **4c,** 15638-08-1; **4d,** 7372-87-4; **5a,** 103-29-7; **5b,** 538-39-6; **5c,** 1657-55-2; **5d,** 952-80-7; **6a,** 776-35-2; **6b,** 69795-81-9; **6c,** 69832-49-1; **6d,** 69795-82-0; **7,** 1587-22-0; **9,** 1812-51-7; *p,p'*-dimethylbenzoin, 1218-89-9; *o,o'*-dimethylbenzoin, 4389-39-3; *p*-tolualdehyde, 104-87-0; *o*-tolualdehyde, 529-20-4; 2-iodobiphenyl, 2113-51-1; acetaldehyde, 75-07-0; 1-biphenylethanol, 16927-84-7.

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Electrolytic Decarboxylation Reactions. 4. Electrosyntheses of 3-Alkyl-2-cycloalken-1-ol Acetates from 1-Alkyl-2-cycloalkene-1-carboxylic Acids. Preparation of *dl*-Muscone from Cyclopentadecanone

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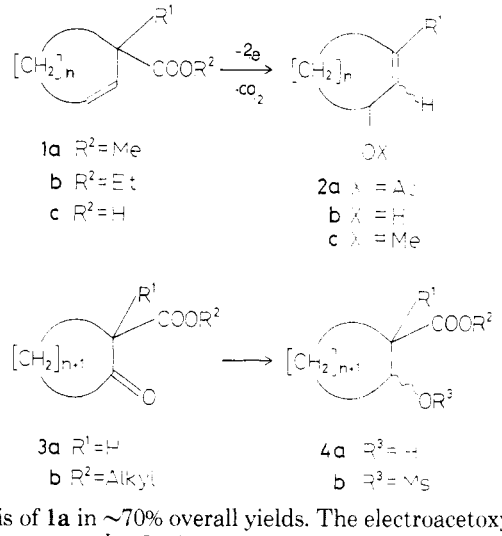
Based on stimulating results on the electrolytic acetoxylation of aliphatic carboxylic acids,[1] we have developed an electrosynthetic procedure for 3-alkyl-2-cycloalken-1-ol acetates (**2a**) from 1-alkyl-2-cycloalkene-1-carboxylic acids (**1c**) prepared from alicyclic 2-oxoalkanoates (**3a**). Synthetic application of such non-Kolbe type reactions on 3-alkenoates has been paid little attention.[2] The present 3-alkyl-2-alken-1-ol synthesis involves a regiospecific acetoxylation at the γ position of the acids **1c**, which serves as an introducing method for a methyl group at the β position of cyclopentadecanone,[3] leading to *dl*-muscone.

The 3-alkenoic acids **1c** were all prepared by (i) alkylation of **3a**, (ii) reduction of **3b** with sodium borohydride or lithium tri-*tert*-butoxyaluminum hydride, (iii) dehydration of the alcohol **4a** via the corresponding mesylate **4b**, and (iv) hydrolysis of **1a** in ~70% overall yields. The electroacetoxylation of **1c** (n = 12, R^1 = Me) was carried out in AcOH–*t*-BuOH–Et_3N using platinum electrodes at a constant applied voltage of ~30 V (36–54 mA/cm², 153 F/mol) at 19–22 °C for 4 h. The electrolysis conditions and results of the related compounds **1c** are shown in Table I.



Electrolytic decarboxylation of the acids **1c** by loss of two electrons on the anode would provide the tertiary carbonium ion a and subsequent three-carbon anionotropic rearrangement[4] of the cation a into the secondary carbonium ion b. The results (Table I) reveal that electrodecarboxylation of **1c** in

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