2,4-dinitrochloronaphthalene. Refluxing time was 2 hr. Purification was achieved by redissolving the filtered crystals in ethanol and precipitating by adding the solution to ice-cold water, yield 96%, mp 73–73.5°. *Anal.* Calcd for $C_{13}H_{13}N_3O_5$: C, 53.70; H, 4.45; N, 14.40. Found: C, 53.75; H, 4.38; N, 14.48. Uv max [2% DMSO–98% H_2O (v/v)] 420 nm[18] (ϵ 7620).[18]

N-Methyl-N-β-hydroxyethyl 2,4-dinitroaniline (5c) was available from a previous study.[12]

Meisenheimer complexes 7a and 7b were prepared by adding a solution of 4 mmol of KOH in 10 ml of ethanol to a solution of 2 mmol of **5a** (**5b**) in 10 ml of ethanol. **7a** was precipitated with cold ether, yield 93%. Recrystallization from ethanol[19] yielded a product decomposing at 298°. *Anal.*[20] Calcd for $C_9H_9N_4O_7K$: C, 33.33; H, 2.80; M, 17.28. Found: C, 32.87; H, 2.91; N, 17.14. Pmr (DMSO-d_6) δ 2.11 (s, 3, CH_3N), 3.24 (m, 2, CH_2N), 4.13 (m, 2, CH_2O), and 8.51 ppm (s, 2, ring); uv max (H_2O) 427 nm (ϵ 22,500). **7b** after crystallization from the reaction solution was filtered and washed with ether *Anal.*[20] Calcd for $C_{13}H_{12}N_3O_5K$: C, 47.42; H, 3.65; N, 12.77. Found: C, 47.32; H, 4.56; N, 12.63. Pmr (DMSO-d_6) δ 1.90 (s, 3, CH_3N), 3.21 (m, 2, CH_2N), 4.25 (m, 2, CH_2O), 8.95 (s, 1, H_3),[21] 8.6 (m, 1, H_8),[21] and 7.3 ppm (broad m, 3, $H_{5,6,7}$);[21] uv max [2% DMSO–98% H_2O (v/v)] 497 nm (ϵ 13,000) and 338 (11,900); uv max (DMSO) 518 nm (ϵ 28,300) and 362 (17,000).

N-Methyl-β-aminoethyl picryl ether hydrochloride (8a) was prepared by rapidly adding 0.5 ml of concentrated HCl to a solution of 730 mg (2.25 mmol) of Meisenheimer complex **7a** in 70 ml of ethanol. KCl precipitated and was filtered off, and the solution was concentrated for crystallization of the product, which was obtained in 76% yield, mp 140°. Recrystallization did not increase the melting point. *Anal.* Calcd for $C_9H_{11}N_4O_7Cl$: C, 33.48; H, 3.44; N, 17.35. Found: C, 33.41; H, 3.53; N, 17.20.

N-Methyl-β-aminoethyl 2,4-dinitronaphthyl ether hydrochloride (8b) was prepared by adding a solution of 300 mg (0.91 mmol) of Meisenheimer complex **7b** in 30 ml of ethanol to 15 ml of ethanolic 0.5 *M* HCl; this latter solution was prepared from HCl gas and ethanol. After the precipitated KCl was filtered off the solution was added to 50 ml of ether, whereupon the product precipitated. For purification the filtered product was redissolved in acidic ethanol and precipitated with ether, yield 50%, mp 180–181°. *Anal.* Calcd for $C_{13}H_{14}N_3O_5Cl$: C, 47.71; H, 4.27; N, 12.84. Found: C, 47.50; H, 4.35; N, 12.71.

N-Methyl-β-aminoethyl 2,4-Dinitrophenyl Ether Hydrochloride (8c).—A 0.25-ml portion of a 14 *M* KOH solution in water was added to 834 mg (3.46 mmol) of *N*-methyl-*N*-β-hydroxyethyl 2,4-dinitroaniline (**5c**) in 2.5 ml of DMSO. The resulting emulsion was added to 10 ml of 1.2 *M* HCl in 90% DMSO. After addition of 4 ml of ethanol most of the KCl precipitated; it was filtered off and the solvent was evaporated at about 40° (0.3 mm). The residue was extracted with ether to remove DMSO and traces of **5c**. The last traces of DMSO were removed by column chromatography with alumina oxide (Baker Analyzed Grade, activity grade I, acid). The ether hydrochloride **8c** was eluted with 0.5 *M* HCl in ethanol. Precipitation with ether, redissolving in acidic ethanol, and reprecipitation with ether yielded a product with mp 182–183°. *Anal.* Calcd for $C_9H_{12}N_3O_5Cl \cdot H_2O$: C, 36.7; H, 4.75; N, 14.25. Found: C, 37.01; H, 4.45; N, 14.12.

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Registry No.—**5a**, 40711-00-0; **5b**, 40711-01-1; **5c**, 37580-86-2; **7a**, 40704-76-5; **7b**, 40704-77-6; **8a**, 40711-03-3; **8b**, 40711-04-4; **8c**, 40711-05-5; *N*-methylethanolamine, 109-83-1; picryl chloride, 88-88-0; 2,4-dinitrochloronaphthalene, 2401-85-6.

(18) From spectrum a in Figure 2. Probably in equilibrium with traces of **8b** as indicated by preliminary kinetic experiments.

(19) The crystallization was very slow. Use of trimethylbenzylammonium ion as gegenion gives better crystallization characteristics.[11]

(20) Meisenheimer complexes notoriously yield poor analyses.

(21) Assignments as for the spiro complex from 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene.[22]

(22) E. J. Fendler, J. H. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 4141 (1968).

Photoreduction of 1,9-Methanodecal-2-ones. Comparison of Cis and Trans Isomers

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Photoreduction of *cis*-1,9-methano-10-methyldecal-2-one (**1c**) occurs with retention of the stereochemistry at C9 to give *cis*-9,10-dimethyldecal-2-one (**3c**); however, photoreduction of the trans isomer **1t** occurs with inversion of the stereochemistry at C9 to also give **3c** as the major product. When the angular methyl group is absent, photoreduction of either isomer occurs with retention of the stereochemistry at C9. A conformational argument is offered as a possible explanation for this difference.

Irradiation (n–π^*) of bicyclo[4.1.0]heptan-2-ones in 2-propanol usually affords cyclohexanones derived from reductive opening of the C1–C7 cyclopropyl bond.[1] Recently, it has been reported that this reaction course can be altered when the bicyclo[4.1.0]-heptan-2-one moiety is part of a decalone or steroidal ketone molecule. Photoreduction of either *cis*- or *trans*-4,5-methanocholestan-3-one gave predominantly *cis*-5-methylcholestan-3-one.[2] Likewise, photoreduction of *trans*-dihydromayurone gave *cis*-8,8,9,10-tetramethyldecal-2-one as one of several products, but no *trans*-8,8,9,10-tetramethyldecal-2-one was found.[3]

From inspection of molecular models, one would *a priori* predict that both *trans*-4,5-methanocholestan-3-one and *trans*-dihydromayurone should photoreduce with retention of the trans stereochemistry. The present study reports the results from photoreduction of a series of isomeric 1,9-methanodecal-2-ones which whould help to elucidate this problem.

The isomeric cyclopropyl ketones were prepared by Simmons–Smith cyclopropylation[4] of the corresponding $\Delta^{1,9}$-octal-2-ols, followed by Jones oxidation.[5] In each case the major alcohol obtained from lithium aluminum hydride reduction of the corresponding

(1) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969).

(2) W. G. Dauben, L. Schutte, and E. J. Deviny, *ibid.*, **37**, 2047 (1972).

(3) G. W. Shaffer, *ibid.*, **37**, 3282 (1972).

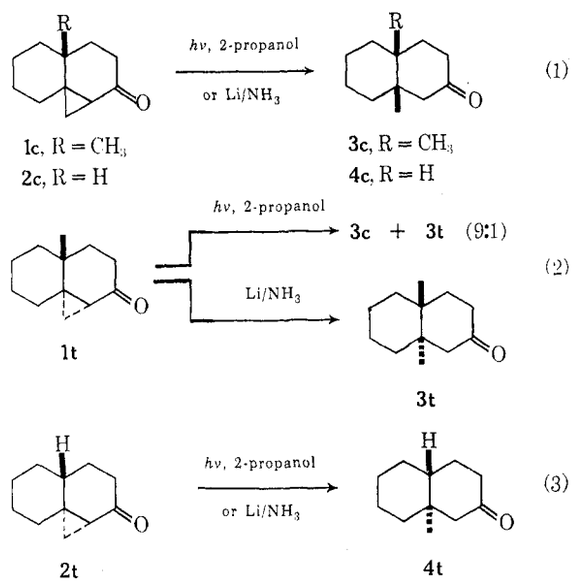
(4) W. G. Dauben, P. Lang, and G. H. Berezin, *ibid.*, **31**, 3869 (1966).

(5) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

enone was assigned the cis stereochemistry.[6] Separation of isomers was accomplished in low yield by chromatography of the cyclopropyl alcohols and/or ketones on alumina.

Photoreduction of *cis*- and *trans*-1,9-methano-10-methyldecal-2-one (**1c**, **1t**) parallels the behavior of the 4,5-methanocholestan-3-ones. Either isomer of **1** gives *cis*-9,10-dimethyldecal-2-one (**3c**) as the predominant product (eq 1 and 2). The small amount of **3t** formed from photoreduction of **1t** could not be isolated and identification was made only on the basis of a glc retention time comparison with **3t** prepared by lithium–ammonia reduction of **1t**. The lithium–ammonia reduction of **1t**, in direct contrast to photoreduction, gives **3t** in good yield (eq 2).

When the bridgehead methyl group is absent (**2c** and **2t**), photoreduction of either isomer parallels lithium–ammonia reduction and the stereochemistry of the cyclopropyl ring is retained in the product (eq 1 and 3).[7]



Irradiation at low temperature (−65°) also reveals a difference between the cis and trans isomers. When the C10 methyl group is present, the trans isomer is stable to prolonged irradiation at 300 nm in 2-propanol, whereas the cis isomer reacts. However, under the same irradiation conditions at 33°, there are no significant differences between **1c** and **1t** in either the quantum yields for disappearance of ketone or formation of product (Table I).

TABLE I

QUANTUM YIELDS FOR DISAPPEARANCE OF KETONE AND FORMATION OF PRODUCT IN 2-PROPANOL[a]

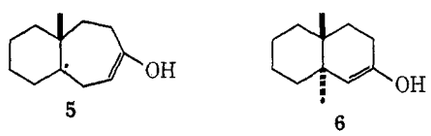
Ketone	Φ_{-k}	Φ (formation of product)
1c	0.50	0.23 (formation of **3c**)
1t	0.74	0.23 (formation of **3c**)
2c	0.45	0.08 (formation of **4c**)
2t	0.38	0.13 (formation of **4t**)

[a] 7–15% disappearance of ketone at 33° using RUL 3000-Å Rayonet lamps.

(6) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 30–32; H. B. Henbest and J. McEntree, *J. Chem. Soc.*, 4478 (1961).

(7) Identical results were obtained for *c*- and *t*-1,9-methano-*t*-6-isopropyl-*r*-(10*H*)-decal-2-one.

The results suggest a conformational control argument as one possible explanation. If the carbonyl group of **1t** should twist 25–30°, which is a maneuver easily accomplished with a Dreiding model, to relieve the 1,3-diaxial interaction of the angular methyl group and the axial hydrogen at C3, then the cyclopropyl ring would bisect the carbonyl p orbital. With this condition, the initial cyclopropyl rupture would occur to give tertiary radical **5** in preference to primary radical **6**.[8] This twisted conformation of **1t** would have



5 6

no effect on the result from lithium–ammonia reduction, since the anion intermediate involved[9] would prefer the primary position leading to **3t**.

Although a 1,3-diaxial interaction similar to that of **1t** exists for **1c** between the C3 hydrogen and the C5 methylene group, a corresponding 25–30° twist of the model carbonyl group is more difficult to accomplish. This nonflexibility of the carbonyl group of **1c**, as compared to **1t**, could allow the carbonyl p orbital to remain aligned for maximum overlap with the outside cyclopropyl bond. Thus, for *cis*-1,9-methano-10-methyldecal-2-ones, the outside cyclopropyl bond opens and the stereochemistry at C9 is retained. This would also be the case for C10 normethyl derivatives where the carbonyl group of the trans isomer would have a lesser tendency to twist owing to the absence of the 1,3-diaxial methyl–hydrogen interaction.

These generalizations are summarized in Chart I.

The failure to observe substantial amounts of cycloheptanone products from either *trans*-4,5-methanocholestan-3-one or **1t** is probably due to the greater hindrance toward hydrogen abstraction of tertiary as compared to primary radicals. When the primary radical is also in a hindered environment, such as exists during photoreduction of the dihydromayurones, then cycloheptanone products are observed.[3]

These experiments do not exclude the possibility that the angular methyl group affects the excited state rather than the ground state conformation.

Experimental Section

Preparative irradiations were carried out with a 450-W medium-pressure Hanovia mercury lamp in a quartz, water-cooled, immersion probe. The filter was a glass cylinder of Corex (>255 nm) insertable between the lamp and the probe. Solutions were outgassed with argon before and during the irradiations.

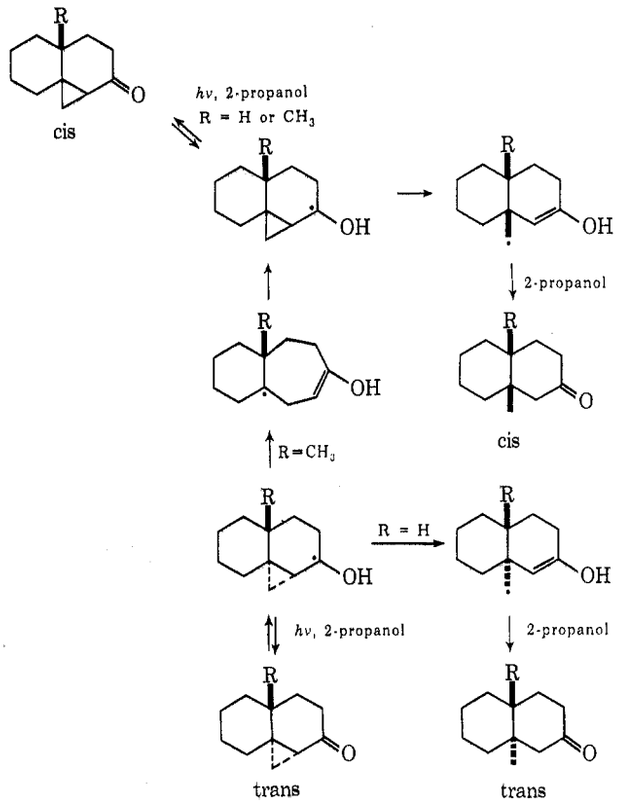
Infrared spectra were taken as neat samples on a Perkin-Elmer 457 and absorptions are reported as inverse centimeters, uv spectra were taken on a Beckman Acta III, nmr spectra were taken on a Varian A-60A as chloroform-d_1 solutions and are reported as δ units relative to TMS, and molecular weights were determined from mass spectra obtained with a Perkin-Elmer 270. Gas–liquid partition chromatography (glpc) was done on a 10% Carbowax 20M (12 ft × 1/8 in.) column. Melting points are uncorrected.

***cis*- and *trans*-1,9-Methano-10-methyldecal-2-one (1c, 1t).—**

(8) W. G. Dauben, G. W. Shaffer, and E. J. Deviny, *J. Amer. Chem. Soc.*, **92**, 6273 (1970).

(9) W. G. Dauben and R. E. Wolf, *J. Org. Chem.*, **35**, 374 (1970).

CHART I



Lithium aluminum hydride reduction of 10-methyl-$\Delta^{1,9}$-octal-2-one gave 85% *cis*- and 15% *trans*-1-methyl-$\Delta^{1,9}$-octal-2-ol.[6] Nester–Faust spinning band distillation (10.0 g) afforded as the first fraction [1.28 g, bp 106–107° (3 mm)] a 1:1 mixture of the cis and trans isomers.

The alcohols (6.00 g, 0.036 mol, 85% cis, 15% trans) were allowed to react under Simmons–Smith conditions[4] to give 1,9-methano-10-methyldecal-2-ol: 85% cis, 15% trans; 3.79 g (58% yield); ir 3350 (s), 1465 (m), 1440 (m), 1040 (m), 962 (m), 925 (m); nmr 4.1–4.5 (1 H, m, α H), 1.00 (cis) (3 H, s, methyl H), 0.35–0.75 (2 H, m, cyclopropyl H), 0.0–0.21 (1 H, m, cyclopropyl H); mass spectrum M^+ (cis) 180, M^+ (trans) 180.

The cyclopropyldecalols were oxidized at 0° with excess Jones reagent[5] to give *cis*- and *trans*-1,9-methano-10-methyldecal-2-one (**1c**, **1t**): ir 1684 (s); nmr 2.03–2.42 (2 H, m, α H), 1.14 (cis), 1.09 (trans) (3 H, 2 s, methyl H), 0.5–1.0 (2 H, m, cyclopropyl H); mass spectrum M^+ (**1c**) 178, M^+ (**1t**) 178; the cis isomer eluted first on glc.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.57; H, 10.10.

Chromatography of the cyclopropyldecalols (4.40 g, 80% cis, 20% trans) on 300 g of alumina (neutral III, 2.5 cm i.d.) gave the pure cis isomer as the first fraction (1.52 g) eluted with benzene–ether (50:1). Oxidation gave pure **1c**.

The Simmons–Smith reaction was repeated on a mixture of 57% *cis*- and 43% *trans*-10-methyl-$\Delta^{1,9}$-octal-2-ol from the above distillation and chromatography on alumina (neutral III, benzene) gave as a later eluted fraction a mixture consisting of 85% *trans*- and 15% *cis*-1,9-methano-10-methyldecal-2-ol. Oxidation of this fraction and rechromatography on alumina (neutral II, benzene) gave a small fraction consisting of 92% **1t** and 8% **1c**.

***cis*- and *trans*-1,9-Methanodecal-2-one (2c, 2t).**—Lithium aluminum hydride reduction of $\Delta^{1,9}$-octal-2-one[10] gave a 3:1 mixture of *cis*- and *trans*-$\Delta^{1,9}$-octal-2-ol.[6]

The alcohols (16.7 g, 0.11 mol) were allowed to react under Simmons–Smith conditions[4] to give 1,9-methanodecal-2-ol: 69% cis, 31% trans; 14.1 g (77% yield); ir 3330 (s), 1440 (m), 1015 (s); nmr 4.1–4.5 (1 H, m, α H), 0.0–0.25 (1 H, m, cyclopropyl H); mass spectrum M^+ (cis) 166, M^+ (trans) 166.

The cyclopropyldecalols were oxidized at 0° with excess Jones reagent[5] to give *cis*- and *trans*-1,9-methanodecal-2-one (**2c**, **2t**): bp 80–82° (0.5 mm); ir 1670 (s), 1440 (m), 1241 (s), 925 (m), 878 (s); nmr 2.01–2.34 (2 H, m, α H), 0.66–1.12 (2 H, m, cyclopropyl H); mass spectrum M^+ 164. The epimeric ketones are inseparable on Carbowax glpc; therefore the isomer ratios were determined by glpc analysis of the precursor alcohols.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.32; H, 9.74.

The cyclopropyldecalols chromatographed twice on alumina (neutral II, ether) gave the pure trans (eluted first) and the pure cis isomer. Each isomer was separately oxidized to give pure **2c** and **2t**.

Photoreduction of *cis*- and *trans*-1,9-Methano-10-methyldecal-2-one (1c, 1t).—The photoreduction of 95% pure **1c** to *cis*-9,10-dimethyldecal-2-one (**3c**) has already been described.[3]

A solution of 0.476 g of a mixture of 53% **1c** and 47% **1t** in 150 ml of 2-propanol (0.018 *M*) was irradiated for 1.3 hr. The solvent was removed under reduced pressure, the residual oil (0.492 g) was oxidized with excess Jones reagent[5] and the resulting mixture (0.467 g) was chromatographed on 125 g of alumina (neutral III, 1.5 cm i.d.).

Benzene first eluted 0.155 g of 85% pure *cis*-9,10-dimethyldecal-2-one (**3c**) (28% yield), which was identified by comparison (nmr spectrum, glpc retention time) with **3c** obtained from lithium–ammonia reduction of **1c**. By glpc and nmr, this fraction contained a very small amount (*ca.* 1% yield) of *trans*-9,10-dimethyldecal-2-one (**3t**). This fraction also contained two other unidentified monomeric products in 4–5% combined yield.

Benzene later eluted 0.148 g (31%) of recovered starting material (1:1 mixture of **1c** and **1t** by nmr and glpc).

Repeating the above irradiation and separation on a mixture of 92% **1t** and 8% **1c** gave the following yields: 27% **3c**, 3% **3t** (identified by glpc retention time only), 41% starting material (94% **1t**, 6% **1c**), 7% of two unidentified monomeric products, and 22% of nonmonomeric material.

Photoreduction of *cis*- and *trans*-1,9-Methanodecal-2-one (2c, 2t).—A solution of 0.207 g of a 1:1 mixture of **2c** and **2t** in 150 ml of 2-propanol (0.008 *M*) was irradiated for 1 hr. The solvent was removed under reduced pressure, the residual oil (0.209 g) was oxidized with excess Jones reagent[5] and the resulting mixture (0.183 g) was chromatographed on 75 g of alumina (neutral III, 1.5 cm i.d.).

Hexane–benzene (4:1) eluted a mixture of *cis*- and *trans*-9-methyldecal-2-one (**4c**, **4t**): 0.059 g (28% yield); ir 1701 (s); nmr 0.97 (s, *cis*-methyl H, 55%), 0.79 (s, *trans*-methyl H, 45%); mass spectrum M^+ 166. This sample was identical (ir and nmr spectra, glpc retention time) with a sample of **4c** and **4t** obtained by lithium–ammonia reduction of a 1:1 mixture of **2c** and **2t**.

Hexane–benzene (1:1) eluted 0.060 g (29%) of unreacted starting material. The remaining 43% was nonmonomeric polar material and was not investigated.

***cis*- and *trans*-9,10-Dimethyldecal-2-one (3c, 3t).**—The preparation and properties of **3c** have already been described.[3] From lithium–ammonia reduction[11] of a mixture of **1c** and **1t** there was obtained a mixture of **3c** and **3t**: ir 1705 (s); nmr 1.22 (trans), 1.03 (cis), 0.95 (trans), 0.91 (cis) (4 s, methyl H); mass spectrum M^+ (cis) 180, M^+ (trans) 180. The two epimers were partially resolved on Carbowax glpc; **3c** eluted first.

***cis*- and *trans*-9-Methyldecal-2-one (4c, 4t).**—From lithium–ammonia reduction[11] of a mixture of **2c** and **2t** there was obtained a mixture of **4c** and **4t**: ir 1705; nmr 0.97 (s, *cis*-methyl H), 0.79 (s, *trans*-methyl H, reported[12] 0.79); mass spectrum M^+ 166.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46: H, 10.91. Found: C, 79.24; H, 10.75.

The two epimers are inseparable on Carbowax glpc. Lithium–ammonia reduction of two different mixtures of **2c** and **2t** (85% **2c**, 15% **2t**; 45% **2c**, 55% **2t**) showed that the **4c**:**4t** ratio could be determined by relative integrations of the two methyl nmr singlets.

Low Temperature Irradiations.—Quartz tubes containing solutions of the various ketones in 2-propanol were immersed in a

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(11) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

(12) J. A. Marshall and H. Roebke, *ibid.*, **34**, 4188 (1969).

methanol bath in a nonsilvered dewar flask which was cooled by circulation of methanol through an external Dry Ice–methanol mixture. The temperature range of the bath was −60 to −68°. The dewar flask was placed in the center of a Rayonet photochemical reactor and irradiated with 8-RUL 3000-Å lamps.

The following results were obtained: *cis*-dihydromayurone[3] in 22 hr gave 16% 7,11,11-trimethylbicyclo[5.4.0]-1-undecan-4-one and 4% *cis*-8,8,9,10-tetramethyldecal-2-one; *trans*-dihydromayurone[3] in 22 hr gave no detectable reaction by glpc; **1c** in 21 hr gave 12% **3c**; **1t** (91% pure) in 21 hr gave no detectable reaction by glpc; **2c** and **2t** (*ca.* 1:1 mixture) in 36 hr, after oxidation with Jones[5] reagent, gave 4% of **4c** and **4t** (1:1). In the case of **2**, the product was isolated and the presence of both **4c** and **4t** shown by the δ 0.97 (**4c**) and 0.79 (**4t**) methyl group nmr singlets. In all the other low temperature irradiations, the percentages were obtained by glpc analysis only.

Quantum Yield Determinations.—Quantum yields were determined according to the procedure of Wagner.[13] Separate solutions of **1c** (0.07 *M*), **1t** (0.07 *M*), **2c** (0.1 *M*), and **2t** (0.1 *M*) in 2-propanol containing octadecane as an internal standard were placed in 1.1-cm Pyrex tubes (each in triplicate), degassed, sealed, and irradiated in parallel at 33° on a merry-go-round using 8-RUL 3000-Å Rayonet lamps. At this concentration, the ketones absorbed >99% of the 300-nm radiation. The amount of ketone that disappeared was measured by glpc analysis (5% Carbowax 20M, 18 ft × 1/8 in.) by comparing the ketone/standard area ratios before and after irradiation. The quantum yields for disappearance (7–15%) of ketone follow: **1c**, 0.50; **1t** (92% pure, 8% **1c**), 0.74; **2c** 0.45; **2t**, 0.38.

The amount of product formed during the irradiation was measured by comparison of glpc peak height to a graph of peak height *vs.* known concentrations of the respective product, using constant volume injections. The quantum yields for product formation follow: **3c** from **1c**, 0.23; **3c** from **1t**, 0.23; **4c** from **2c**, 0.08; **4t** from **2t**, 0.13.

Two tubes containing 1.0 *M* acetone and 0.20 *M* *cis*-1,3-pentadiene in cyclohexane were irradiated in parallel with the above samples. The average yield (10%) of *trans*-1,3-pentadiene was measured by comparison of glpc (10% UCW 98, 18 ft × 1/8 in.) peak height to a graph of peak height *vs.* known concentrations of *trans*-1,3-pentadiene in the above solution of *cis*-1,3-pentadiene, acetone, and cyclohexane, using constant volume injections. The quantum yield for the cis to trans isomerization, after being corrected for back reaction, is 0.555.[14]

Acknowledgments.—The author would like to thank W. G. Dauben and A. R. Hochstetler for helpful discussions regarding this research, P. Shubiak for glpc analyses related to the quantum yield determinations, and J. Fischer for excellent technical assistance.

Registry No.—**1c**, 35340-22-8; **1t**, 40447-74-3; **2c**, 40447-75-4; **2t**, 40447-76-5; **3c**, 5523-99-9; **3t**, 40447-78-7; **4c**, 2530-17-8; **4t**, 1197-95-1; 10-methyl-$\Delta^{1,9}$-octal-2-one, 826-56-2; *cis*-10-methyl-$\Delta^{1,9}$-octal-2-ol, 31654-83-8; *trans*-10-methyl-$\Delta^{1,9}$-octal-2-ol, 40447-83-4; *cis*-1,9-methano-10-methyldecal-2-ol, 13903-60-1; *trans*-1,9-methano-10-methyldecal-2-ol, 40447-85-6; $\Delta^{1,9}$-octal-2-one, 1196-55-0; *cis*-$\Delta^{1,9}$-octal-2-ol, 30983-79-0; *trans*-$\Delta^{1,9}$-octal-2-ol, 2763-42-0; *cis*-1,9-methanodecal-2-ol, 40447-89-0; *trans*-1,9-methanodecal-2-ol, 40447-90-3.

(13) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

(14) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

Mono- and Disubstituted Vinyltrialkylammonium Compounds. Synthesis and Stereochemistry

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Methyl propiolate reacts with trimethyl-, triethyl-, tri-*n*-butylammonium, and pyridinium halide salts in water–dioxane to yield *trans*-methoxycarbonylvinyltrialkylammonium salts. Similarly, dimethyl acetylenedicarboxylate adds trimethyl- and triethylammonium halide salts to produce the *cis*-bis(methoxycarbonyl)-vinyltrialkylammonium compounds. Other disubstituted vinyltrimethylammonium salts were prepared by dehydrobromination of 1,1,2-tribromoethyltrimethylammonium bromide and 2-carboxy-1,2-dibromoethyltrimethylammonium bromide to yield the respective (*E*)-dibromovinyltrimethylammonium and (*E*)-1-bromo-2-carboxyvinyltrimethylammonium bromides. The stereochemistry and chemical shift assignment of both the mono- and disubstituted vinylammonium salts were established using the additivity relationship developed by Matter and Tobey, $\delta_{C=CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$. The shielding parameters for the trialkylammonium substituent were determined to be $Z_{gem} = 1.00$, $Z_{cis} = 0.65$, and $Z_{trans} = 0.30$. A reinvestigation of the reaction of 1-bromovinyltrimethylammonium bromide with $NaOCH_3$ or KOC_2H_5 revealed that the isomeric *cis*-alkoxyvinyltrimethylammonium bromide is also formed in addition to the reported 1-alkoxyvinyltrimethylammonium bromide.

The synthesis of vinyltrimethylammonium compounds is well documented. In most cases they are prepared by addition of aqueous trimethylamine to acetylene or monosubstituted acetylenic derivatives.[1–3] Until 1969, there were few reports on the synthesis of vinyltrialkylammonium salts containing an alkyl group other than methyl. With ethoxyacetylene, Arens[2] found that aqueous solutions of triethyl- or tri-*n*-butylamine reacted sluggishly or not at all. In an improved modification of Reppe's[1] neurine synthesis, Fisher[4,5] succeeded in preparing a series of *N*-(2-formylvinyl)trialkylammonium salts by treating a mineral acid salt of a tertiary amine with propiolaldehyde. With few exceptions, these and other 2-monosubstituted vinyltrialkylammonium salts have been shown by nmr spectroscopy to possess a trans configuration.[4–7]

Other monosubstituted vinyltrimethylammonium salts have been synthesized either by dehydration[8] or

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