Photochemistry of Some Heterocyclic Analogues of 3,3,5,5-Tetramethylcyclohexanone

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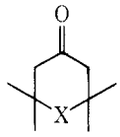
Received June 7, 1977

The photolysis of tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-4-one (**1**), 2,2,6,6-tetramethyl-4-piperidone (**2**), tetrahydro-2,2,6,6-tetramethyl-4*H*-thiopyran-4-one (**3**), and 3,3,5,5-tetramethylcyclohexanone (**4**) was investigated in methanol and 2-propanol. The main products formed in the irradiation of **1** and **2** were the pinacol dimers octahydro-2,2,2′,2′,6,6,6′,6′-octamethyl[4,4′-bi-4*H*-pyran]-4,4′-diol (**5**) and 2,2,2′,2′,6,6,6′,6′-octamethyl[4,4′-bipiperidine]-4,4′-diol (**9**), respectively, while **3** gave primarily the photoreduced product, tetrahydro-2,2,6,6-tetramethyl-2*H*-thiopyran-4-ol (**12**). The principal reaction of compound **4** on irradiation in methanol was a Norrish type I cleavage to yield methyl 3,3,5,5-tetramethylhexanoate (**14**).

The photolysis of tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-3-one in methanol has been shown to yield 2,2-dimethyl-5-methoxytetrahydrofuran.[1] The formation of this ring contraction product was postulated to arise via an oxacarbene intermediate, although it could also be explained by direct cleavage of the starting material into acetone and 2,2-dimethylcyclobutanone from which 2,2-dimethyl-5-methoxytetrahydrofuran is known to form on photolysis.[2]

To determine the scope of this reaction we examined the photolysis of the related heterocyclic systems **1, 2,** and **3** and their carbocyclic analogue **4** in methanol and 2-propanol. After

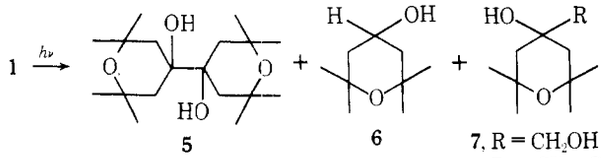


1, X = O
2, X = NH
3, X = S
4, X = CH_2

each photolysis, the reaction mixture was examined by gas chromatography and combined gas chromatography–mass spectrometry in order to obtain quantitative and qualitative information on the products formed.

Results

The irradiation of **1** in methanol afforded octahydro-2,2,2′,2′,6,6,6′,6′-octamethyl[4,4′-bi-4*H*-pyran]-4,4′-diol (**5**) as the major product. The remaining products were tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-4-ol (**6**) and tetrahydro-

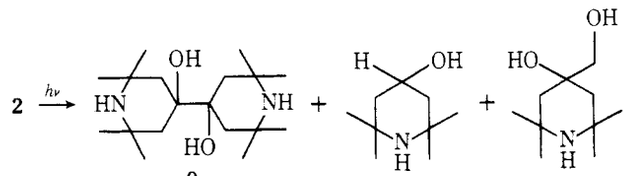


5 **6** **7**, R = CH_2OH; **8**, R = $(CH_3)_2COH$

4-hydroxy-2,2,6,6-tetramethyl-4*H*-pyran-4-methanol (**7**). The structure of **5** was supported by its analytical data and its infrared, nuclear magnetic resonance, and high-resolution mass spectra. Compound **6** was identified by comparison of its properties and spectra with those of an authentic sample prepared by lithium aluminum hydride reduction of **1**. The structure of **7** was obtained from spectral data.

The photolysis of **1** in 2-propanol also gave **5** and **6** in addition to the mixed pinacol tetrahydro-4-hydroxy-α,α,2,2,6,6,-hexamethyl-4*H*-pyran-4-methanol (**8**), which was identified from its spectral data.

When **2** was irradiated in methanol, 2,2,2′,2′,6,6,6′,6′-octamethyl[4,4-bipiperidine]-4,4′-diol (**9**), 4-hydroxy-2,2,6,6-tetramethylpiperidine (**10**), and 4-hydroxy-2,2,6,6-tetramethyl-4-piperidinemethanol (**11**) were obtained. Compounds **9** and **11** were identified from their spectral data, and the



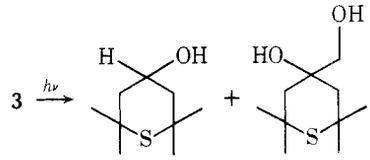
9 **10** **11**

structure of **10** was established by comparison of its physical and spectral properties with those of an authentic sample.

The irradiation of **2** in 2-propanol gave results similar to those obtained in the irradiation of **1**.

When **3** was irradiated in methanol, tetrahydro-2,2,6,6-tetramethyl-2*H*-thiopyran-4-ol (**12**) and tetrahydro-4-hydroxy-2,2,6,6-tetramethyl-2*H*-thiopyran-4-methanol (**13**) were the only products isolated by preparative gas chromatography. Compound **12** was identified by comparison of its physical properties with those of an authentic sample prepared by lithium aluminum hydride reduction of **3**. The structure of **13** was established from its spectral data. Ring contraction products had been previously reported[3] for the photolysis of **3** and other tetrahydrothiopyranones in *tert*-butyl alcohol, but no such products could be detected under our experimental conditions.

The photolysis of **3** in 2-propanol afforded compound **12** (84%) as the main product.



12 **13**

Although the photolysis of **4** in methanol had previously been investigated by Hagens,[4] we repeated the experiment and confirmed the products reported by Hagens: methyl 3,3,5,5-tetramethylhexanoate (**14**), 2,2,4,4,10,10,12,12-octamethyl-7,14-dioxadispiro[5.1:5.2]pentadecane (**15**), 1-hydroxy-3,3,5,5-tetramethylcyclohexanemethanol (**16**), and 3,3,5,5-tetramethylcyclohexanol (**17**).

Hagens[4] suggested that **15** could arise via the condensation of **4** with the mixed pinacol 1-hydroxy-3,3,5,5-tetramethylcyclohexanemethanol (**16**) in a ground-state acid-catalyzed reaction. We found that compounds **14** and **15** were the major

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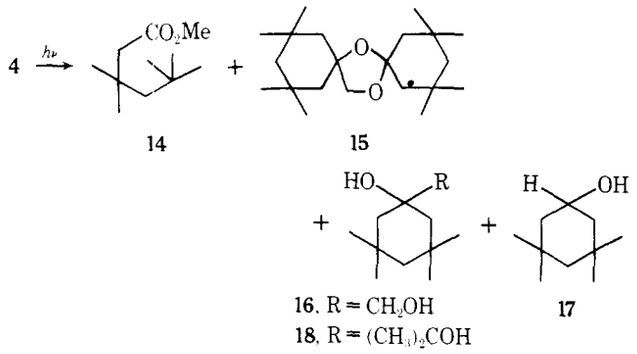
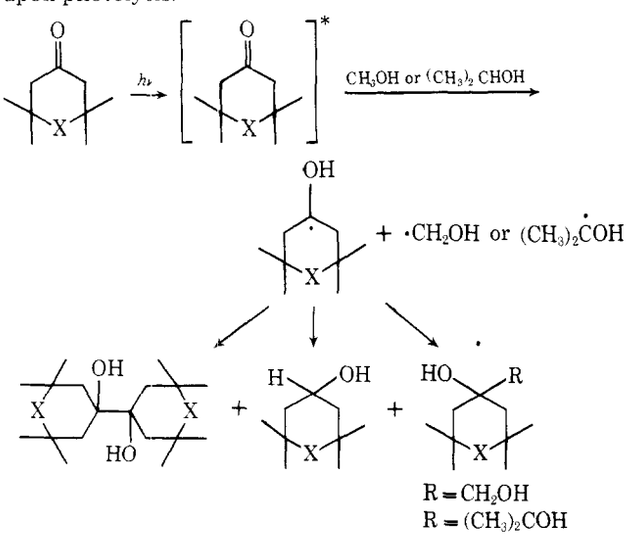
products formed along with smaller amounts of 1-hydroxy-3,3,5,5-tetramethylcyclohexanemethanol (**16**). Compound **15** precipitated from solution and was identified via its mass spectral fragmentation data as well as by comparing its physical and spectral properties to the literature values reported by Hagens.[4] The filtrate was resolved by preparative gas chromatography. Compounds **14, 16, and 17** were identified from their spectral data and by comparison of their physical properties to the literature values of the products obtained by Hagens.[4]

In 2-propanol, the major photolysis product was **17.** A small amount of 1-hydroxy-$\alpha,\alpha,3,3,5,5$-hexamethyl-1-cyclohexanemethanol (**18**) was also observed.

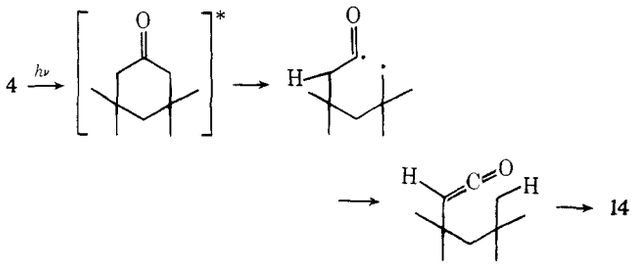


Discussion

The photolysis of either tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-4-one (**1**) or its piperidone analogue (**2**) in methanol or 2-propanol resulted in the formation of the corresponding pinacols **5** and **9** as the major reaction products. Conversely, the photolysis of **3** and **4** under similar conditions gave the respective pinacols, but as minor products which could only be detected by combined gas chromatograhpy–mass spectrometry. These products were tentatively identified from their mass spectral fragmentation patterns which were similar to those of **5** and **9.** The principal products from the irradiation of **3** in either methanol or 2-propanol or **4** in 2-propanol were the corresponding alcohols **12** and **16,** respectively, suggesting that photoreduction was the predominant reaction pathway in these photolyses. Only compound **4** underwent a Norrish type I cleavage to afford ester products, this process being the major decomposition pathway in methanol. No evidence of ring contraction or of a Norrish type I cleavage could be detected in the photolysis of any of the six-membered heterocyclic ketones studied (**1, 2,** and **3**). These observations are in direct contrast with the behavior of tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-3-one, which exhibited both processes upon photolysis.[1]



All of the products formed upon irradiation of heterocyclic ketones **1–3** were the result of a hydrogen transfer process between the solvents, methanol or 2-propanol, and the excited state of the ketone to yield a ketyl radical.[5] The ketyl radical, in turn, could abstract another hydrogen atom from the solvent to give the photoreduced products (**6, 10,** and **12**) or could couple to afford the corresponding pinacol dimers as major reaction products (**5** and **9**). Finally, the ketyl radical could react with solvent-based radicals to give mixed pinacols (**7, 8, 11, 13, 16,** and **18**). The mixed pinacols, 4-hydroxy-$\alpha,\alpha,2,2,6,6$-hexamethylpiperidone-4-methanol and tetrahydro-4-hydroxy-$\alpha,\alpha,2,2,6,6$-hexamethyl-2*H*-thiopyran-4-methanol, were also found to occur in trace amounts and were tentatively identified by comparison of their mass spectral fragmentation patterns to those of **8** and **18.**[6]



Although **4** underwent reduction and dimerization reactions similar to those of its heterocyclic analogues **1, 2,** and **3,** it also decomposed via a Norrish type I cleavage.

The fact that the heterocyclic analogues of **4** (**1, 2,** and **3**) did not undergo a Norrish type I cleavage is of some interest. This behavior is not only in contrast with that of **4** but also with that of other heterocyclic ketones such as 2,2,4,4-tetramethyl-3-oxetanone,[7] 2,2,5,5-tetramethyldihydro-3-furanone,[8] and tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-3-one,[1] which predominantly undergo Norrish type I cleavage on irradiation under similar conditions. The nature of the solvent appears to be of great importance in these reactions since irradiation of **3** in *tert*-butyl alcohol yielded products which resulted primarily from a Norrish type I cleavage.[3] In a nonprotic solvent such as acetonitrile, no reaction occurred.[9]

The Norrish type I cleavage of compounds **1–4,** in contrast with those of oxaheterocyclic ketones previously investigated,[1,7,8] would yield a primary radical which, although possessing some stability in the carbocyclic analogue **4,** could be further destabilized by the heteroatoms present in **1, 2,** and **3.** Therefore, α cleavage in these compounds should be highly reversible and should allow hydrogen abstraction to compete successfully.[10] However, other factors may be involved. It is also plausible that the 4-heteroatoms stabilize the excited state in such a way that compounds **1–3** react from the excited state before cleavage can occur.

Experimental Section

Melting points were taken on a Mel-Temp or Thomas Hoover Unimelt apparatus and are uncorrected. Preparative VPC separations were carried out on an Aerograph 700 chromatograph equipped with 12 ft × 0.25 in stainless steel columns containing Carbowax 20M (15%) and/or a column containing SE-30 (15%) on 45–60 mesh Chromosorb W. Yields are based on gas chromatographic analysis with the balance of the mixture consisting of unreacted starting material. ^{1}H NMR spectra were recorded on Varian A-60A, Varian HA-100, or Varian HR-220 spectrometers using Me_4Si as an internal standard. Combined gas chromatography–mass spectrometry was carried out using a Perkin-Elmer 990 gas chromatograph interfaced to a Hitachi RMU-6L mass spectrometer via a Watson–Biemann separator.[11] The gas chromatograph was equipped with a flame ionization detector and a 10 ft × 2 mm (i.d.) 3% XE-60 glass column to separate the reaction mixtures. Chromatographic conditions were as follows: He flow rate, 30 mL/min; temperature program, 60 °C (4 min) to 230 °C at 6 °C/min; injector 290 °C and detector 250 °C. Conditions for the mass

spectrometer were as follows: 70-eV ionizing potential; ion source temperature 200 °C and interface temperature, 250 °C. High-resolution spectra are recorded on a CEC-110B mass spectrometer using photoplate recording. The spectra were run at the Mass Spectrometry Laboratory at Massachusetts Institute of Technology, Professor Klaus Biemann, director. Ultraviolet spectra were obtained on a Beckman DBG spectrophotometer. Infrared spectra were taken on a Perkin-Elmer 137 Infracord or a Perkin-Elmer 521 spectrophotometer. Microanalyses were performed by Midwest Microlabs, Ltd., Indianapolis, Ind.

Starting Materials. 2,2,6,6-Tetramethyl-4-piperidone (**2**) and 3,3,5,5-tetramethylcyclohexanone (**4**) were commercially available. Compound **4** was used without further purification, and **2** was purified by sublimation. The procedure of Korobitsyna and Pivnitskii,[12] as modified by Wasacz,[13] was used to prepare **1**, and a similar procedure by Naylor[14] was used to prepare **3**, both in low yields. Preparative gas chromatography yielded **1** and **3** in greater than 99.9% purity.

Tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-4-one (1). 2,6-Dimethyl-2,5-heptadien-4-one (Phorone) (20 g, 0.195 mol) was placed in a 100-mL, two-necked, round-bottomed flask equipped with a condenser, a magnetic stirring bar, and a gas inlet tube. The flask was cooled in an ice bath, and hydrogen chloride was bubbled through the stirred ketone for 2 h. The reaction mixture was allowed to stand overnight and was then washed with water. The oil that separated was treated with 100 mL of water, saturated with sodium chloride, and extracted three times with 30 mL of diethyl ether. The ether extracts were dried with anhydrous magnesium sulfate, filtered, and distilled at atmospheric pressure to remove the solvent. The residue was combined with an equal volume of saturated sodium bisulfite solution, and the mixture was stirred magnetically overnight. The white crystalline solid that formed was collected by filtration, washed with ether, air-dried, and then treated with sufficient 20% aqueous sodium hydroxide solution to dissolve the solid. The oil that separated was chromatographically pure tetra-2,2,6,6-tetramethyl-4*H*-pyran-4-one (**1**): 3.39 g, 15% yield; lit.[12] bp 62.5–63.5 °C (11 mm); IR (CCl_4) 3000, 1720, 1380, 1365, 1295, 1225 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 6 H,), 1.38 (s, 6 H), 2.49 (s, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 156 (M^+, 3), 141 (95), 98 (52), 85 (79), 83 (100), 70 (52), 56 (84).

2,2,6,6-Tetramethyl-4-piperidone (2). This compound was sublimed at its melting point: mp 56 °C (lit.[15] mp 58–59 °C); IR (KBr) 3320, 2960, 1687, 1450, 1285, 1210 cm^{-1}; NMR (CCl_4) δ 1.23 (s, 12 H), 1.52 (br s, 1 H), 2.25 (s, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 155 (M^+, 18), 140 (100), 112 (20), 98 (67), and 83 (99); UV λ_{max} 245 nm (ϵ 14).

Tetrahydro-2,2,6,6-tetramethyl-4*H*-thiopyran-4-one (3). In a 125-mL, two-necked, round-bottomed flask equipped with a condenser, a gas inlet tube, and a gas outlet adapter attached to the top of the condenser leading to a trap containing a potassium hydroxide solution was placed 20 g (0.145 mol) of 2,6-dimethyl-2,5-heptadien-4-one (Phorone), 80 mL of 95% ethanol, and 0.4 g (0.007 mol) of potassium hydroxide. The solution was heated to reflux, and hydrogen sulfide was bubbled through it for 7 h. The resulting mixture was then cooled, diluted with an equal volume of water to give a two-phase system, and extracted with three 40-mL portions of diethyl ether. The combined ether extracts were dried with anhydrous magnesium sulfate, filtered, and evaporated. The residue was distilled in vacuo to give 15.5 g of product (62.1% yield), bp 90–95 °C (13 mm) [lit.[3] bp 96 °C (8 mm)]. Treatment of the product with 15.5 g of semicarbazide hydrochloride afforded 17.9 g of the corresponding semicarbazone (86.9% yield). The semicarbazone (12.5 g, 0.0545 mol) was hydrolyzed by refluxing it in 125 mL of 2 N hydrochloric acid for 30 min. The oil that separated was extracted with ether (3 × 20 mL). The extracts were dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to yield 7.1 g of the chromatographically pure ketone (56.7% yield): lit.[3] bp 92 °C (14 mm); IR (neat) 2910, 1705, 1440, 1380, 1290, 1210 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (s, 12 H), 2.55 (s, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 172 (M+, 91), 157 (76), 129 (9), 117 (65), 101 (61), 89 (54), 83 (100), 75 (81), 74 (93); UV λ_{max} 253 nm (ϵ 3.3).

3,3,5,5-Tetramethylcyclohexanone (4). This compound was commercially available: lit.[16] bp 79 °C (12 mm); IR (neat) 2950, 2910, 1705, 1450, 1380, 1360, 1340, 1275, 1220 cm^{-1}; NMR ($CDCl_3$) δ 1.03 (s, 12 H), 1.58 (s, 2 H), 2.15 (s, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 154 (M^+, 56), 139 (58), 126 (8), 111 (6), 97 (56), 83 (100), 56 (57), 55 (65); UV λ_{max} 288, 243 nm [lit.[16] λ_{max} 286 (ϵ 20)].

Photochemical Studies. The photolysis of **1** was carried out using a Hanovia 450-W, type L, high-pressure, mercury-arc lamp in a water-cooled, unfiltered quartz immension well. Special grade solvents were used for all photolyses and analyzed by VPC prior to use. All solutions were irradiated with stirring in a nitrogen atmosphere. Compounds **2, 3,** and **4** were irradiated in a quartz cell positioned at the center of a helical Hanovia, low-pressure, mercury-arc lamp.

A. Irradiation of Tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-4-one (1) in Methanol. When compound **1** (3.0 g, 0.0192 mol) was irradiated in 10 mL of methanol for 48 h, compound **5** (41%) precipitated from solution and was removed by filtration. The remaining products, **6** (11%) and **7** (5%), were isolated by preparative gas chromatography. An additional compound detected in the chromatogram was tentatively identified as octahydro-2,2,4,4,10,10,12,12-octamethyl-3,7,11,14-tetraoxadispiro[5.1:5.2]pentadecane, the pyran analogue of **15.** This tentative identification is based on the similarity of its mass spectral fragmentation pattern with that of **15.**[6]

B. Irradiation of 1 in 2-Propanol. Compound **1** (2.0 g, 0.0128 mol) in 6 mL of 2-propanol was irradiated as in A to give **5** (38%), **6** (13%), and **8** (6%).

C. Irradiation of 2,2,6,6-Tetramethyl-4-piperidone (2) in Methanol. Compound **2** (2.0 g, 0.0129 mol) was irradiated in 10 mL of methanol for 72 h to give **9** (36%), which precipitated from solution and was removed by filtration. Compounds **10** (18%) and **11** (5%) were isolated by preparative gas chromatography.

D. Irradiation of 2 in 2-Propanol. Compound **2** (3.0 g, 0.0193 mol) in 15 mL of 2-propanol was irradiated as in C to give **9** (25%). An additional compound detected in the chromatogram was tentatively identified as 4-hydroxy-α,α,2,2,6,6-hexamethylpiperidinemethanol, the nitrogen analogue of **8.** This tentative identification is based on the similarity of its mass spectral fragmentation pattern with that of **8.**[6]

E. Irradiation of Tetrahydro-2,2,6,6-tetramethyl-4*H*-thiopyran-4-one (3) in Methanol. Compound **3** (1.5 g, 0.0087 mol) in 10 mL of methanol was irradiated for 48 h to give **12** (27%) and **13** (4%).

F. Irradiation of 3 in 2-Propanol. Compound **3** (1.5 g, 0.0087 mol) in 10 mL of 2-propanol was irradiated as in E to give **12** (85%) and **13** (1%), and two additional compounds detected in the chromatogram were tentatively identified as tetrahydro-α,α,2,2,6,6-hexamethyl-2*H*-thiopyran-4-methanol and octahydro-2,2,2′,2′,6,6,6′,6′,-octamethyl[4,4′-bi-2*H*-thiopyran]-4,4′-diol, the sulfur analogues of **8** and **5.** This tentative identification is based on the similarity of their mass spectral fragmentation patterns to those of **8** and **5.**[6]

G. Irradiation of 3,3,5,5-Tetramethylcyclohexanone (4) in Methanol. Compound **4** (5 g, 0.032 mol) in 15 mL of methanol was irradiated for 72 h to afford **14** (29%), **15** (24%), **16** (14%), and **17** (7%). Very small amounts of two additional products detected in the chromatogram were tentatively identified as 3′,3′,5′,5′-tetramethylcyclohexyl-3,3,5,5-tetramethylhexanoate and 3,3,3′,3′,5,5,5′,5′-octamethyl[1,1′-bicyclohexane]-1,1′-diol. This tentative identification is based on the similarity of their mass spectral fragmentation patterns to the products isolated in the photolyses of **1** and **2.**[6]

H. Irradiation of 4 in 2-Propanol. Compound **4** (5 g, 0.032 mol) in 15 mL of 2-propanol was irradiated as in G to give **17** (24%) and **18** (5%). Small amounts of the two products tentatively identified in G were also noted. Only a trace of the expected 2-propyl-3,3,5,5-tetramethylhexanoate, tentatively identified from its mass spectral fragmentation pattern, was observed in the photolysis mixture.[6]

Authentic samples of alcohols **6, 10, 12,** and **17** were prepared by lithium aluminum hydride reduction of the starting ketones **1** and **4.** The general procedure is illustrated with the preparation of tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-4-ol (**6**).

Tetrahydro-2,2,6,6-tetramethyl-4*H*-pyran-4-ol (6). Lithium aluminum hydride (1 g, 0.026 mol) was stirred in 15 mL of ether in a 50-mL, two-necked flask equipped with a dry ice condenser and a pressure-equalizing dropping funnel. Compound **1** (0.5 g, 0.0032 mol) in 10 mL of ether was added through the dropping funnel over a period of 5 min. The mixture was refluxed for 30 min, allowed to cool to room temperature (~15 minutes), and then slowly hydrolyzed with water (20 mL). The solution was filtered, and the filtrate was separated. The aqueous layer was extracted with ether (3 × 10 mL). The ether extracts were combined with the separated ether layer. The ether was dried with $MgSO_4$ and filtered and the ether evaporated to yield **6** as white crystals (0.494 g, 97.5% yield): mp 82–83 °C; IR (KBr) 3225, 2900, 1450, 1360, 1165 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (s, 6 H), 1.29 (s, 6 H), 1.41 (d, J = 9 Hz, 2 H), 2.58 (s, 1 H), 4.09 (m, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 143 (82), 125 (96), 107 (56), 87 (88), 59 (100). Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.11; H, 11.59.

4-Hydroxy-2,2,6,6-tetramethyl-4-piperidine (10): mp 127–128 °C (lit.[15] mp 128–128.5 °C); IR (KBr) 3335, 3195, 2875, 1370, 1355, 1050 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (s, 6 H), 1.21 (s, 6 H), 1.92 (dd, $\Delta\nu$ = 6 Hz, J = 4 Hz, 4 H), 2.26 (s, 1 H), 4.05 (m, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 157 (M^+, 3), 142 (99), 124 (39), 107 (19),

98 (67), 86 (58), 83 (62), 59 (100).

Tetrahydro-2,2,6,6-tetramethyl-2*H*-thiopyran-4-ol (12): mp 65–66 °C (lit.[5] mp 67 °C); IR (KBr) 3250, 2940, 2880, 1460, 1140, 1040 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 6 H), 1.43 (s, 6 H), 1.81 (s, 1 H), 2.00 (dd, $\Delta\nu$ = 6 Hz, J = 2 Hz, 4 H), 3.98 (m, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 174 (M^+, 89), 159 (84), 141 (21), 140 (19), 125 (57), 99 (38), 98 (19), 85 (79), 75 (74), 69 (100).

3,3,5,5-Tetramethylcyclohexanol (17): mp 83–84 °C (lit.[4] mp 82–84 °C); IR (CCl_4) 3610, 3335, 2920, 1475, 1460, 1385, 1360, 1050 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (d, J = 10 Hz, 12 H), 1.03–1.24 (complex), 1.73 (d, J = 6 Hz, 4 H), 3.91 (m, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 155 (3), 154 (6), 141 (7), 138 (32), 123 (100), 97 (64), 95 (57), 85 (72), 83 (57), 82 (52), 81 (82), 67 (55).

Octahydro-2,2,2′,2′,6,6,6′,6′-octamethyl[4,4′-bi-4*H*-pyran]-4,4′-diol (5): mp 154–155 °C; IR (KBr) 3520, 3360, 2970, 2925, 1450, 1370, 1360, 1120 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (s, 12 H), 1.44 (s, 12 H), 1.45 (d, J = 6 Hz, 4 H), 1.69 (d, J = 6 Hz, 4 H), 2.26 (s, 2 H); mass spectrum (Figure 1, Supplementary Material) (70 eV), *m/e* relative intensity) 299 (4; elemental composition $C_{17}H_{31}O_4$), 281 (39), 263 (22), 207 (25), 205 (22), 158 (56), 140 (63), 125 (78), 99 (100). Anal. Calcd for $C_{18}H_{34}O_4$: C, 69.24; H, 11.04. Found: C, 69.25; H, 11.01.

Tetrahydro-4-hydroxy-2,2,6,6-tetramethyl-4*H*-pyran-4-methanol (7): IR (KBr) 3475, 2985, 2890, 1385, 1370, 1235, 1170 cm^{-1}; NMR ($CDCl_3$) δ 1.22 (d, J = 8 Hz, 12 H), 1.44 (s, 2 H), 1.65 (br s, 4 H), 1.99 (br s, 1 H), 3.75 (s, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 173 (70), 157 (11), 155 (89), 137 (75), 99 (100), 95 (95). Anal. Calcd for $C_{10}H_{20}O_3$: C, 64.48; H, 9.74. Found: C, 64.33; H, 9.96.

Tetrahydro-4-hydroxy-α,α,2,2,6,6-hexamethyl-4*H*-pyran-4-methanol (8): IR (KBr) 3450, 3335, 1460, 1375, 1360, 1155 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (s, 12 H), 1.45 (s, 6 H), 1.71 (br s, 4 H), 3.42 (br s, 1 H), 3.68 (br s, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 201 (29), 183 (24), 165 (25), 157 (51), 145 (20), 127 (56), 99 (100), 59 (89).

2,2,2′,2′,6,6,6′,6′-Octamethyl[4,4′-bipiperidine]-4,4′-diol (9): mp 170–172 °C; IR (KBr) 3525, 2960, 2925, 1440, 1370, 1360, 1350, 1110 cm^{-1}; NMR (acetic acid-d_4) δ 1.46–1.50 (br d, 6 H), 1.70 (br s, 6 H), 1.96 (br s, 4 H), 2.16 (s, 1 H); mass spectrum (Figure 2, Supplementary Material) (70 eV) *m/e* (relative intensity) 297 (14; elemental composition $C_{18}H_{36}N_2O_2$), 279 (72), 261 (46), 246 (9), 156 (51), 142 (11), 138 (25), 124 (24), 98 (82), 58 (100).

4-Hydroxy-2,2,6,6-tetramethyl-4-piperidinemethanol (11): IR (CCl_4) 3330, 2900, 2860, 1440, 1365, 1350 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (s, 6 H), 1.19 (s, 6 H), 1.43 (s, 4 H), 2.25 (br s, 1 H), 3.35 (s, 1 H), 3.64 (s, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 187 (M^+, 9), 172 (100), 156 (56), 154 (82), 140 (11), 136 (25), 112 (42), 98 (88).

Tetrahydro-4-hydroxy-2,2,6,6-tetramethyl-2*H*-thiopyran-4-methanol (13): IR (CCl_4) 3400, 2940, 2900, 1460, 1440, 1365, 1070 cm^{-1}; NMR ($CDCl_3$) δ 1.29 (s, 6 H), 1.46 (s, 6 H), 1.59 (br s, 2 H), 2.04 (dd, $\Delta\nu$ = 12 Hz, J = 4 Hz, 2 H), 2.60 (s, 1 H), 2.73 (s, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 204 (M^+, 53), 189 (37), 173 (47), 171 (90), 153 (28), 143 (53), 130 (38), 115 (93), 83 (96), 75 (100).

Methyl 3,3,5,5-Tetramethylhexanoate (14). The spectral properties of this compound agreed with those reported by Hagens:[4] IR (CCl_4) 2980, 2955, 1735, 1470, 1435, 1365, 1230, 1150, 1115 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (s, 9 H), 1.08 (s, 6 H), 1.40 (s, 2 H), 2.25 (s, 2 H), 3.60 (s, 3 H). The structure of this compound was further supported by its mass spectral data: mass spectrum (70 eV), *m/e* (relative intensity) 186 (M^+, 2), 171 (21), 155 (25), 153 (31), 139 (38), 131 (44), 130 (48), 129 (42), 115 (68), 113 (72), 97 (74), 57 (100).

2,2,4,4,10,10,12,12-Octamethyl-7,14-dioxadispiro[5.1:5.2]-pentadecane (15). This compound precipitated during photolysis. It was removed by filtration and recrystallized from 95% ethanol: mp 96–97 °C (lit.[4] mp 96–99 °C); IR (CCl_4) 3015, 2945, 1480, 1455, 1390, 1370, 1350 cm^{-1}; NMR ($CDCl_3$) δ 0.92 (s, 6 H), 1.02 (s, 6 H), 1.13 (s, 2 H), 1.45 (s, 2 H), 3.68 (s, 2 H); mass spectrum (Figure 3, Supplementary Material) (70 eV), *m/e* (relative intensity) 322 (M^+, 1), 307 (6), 251 (85), 197 (3), 195 (2), 168 (13), 151 (81), 109 (58), 83 (100).

1-Hydroxy-3,3,5,5-tetramethylcyclohexanemethanol (16). The spectral properties of this compound agreed with those reported by Hagens:[4] IR (CCl_4) 3500, 3330, 1385, 1365, 1045 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (s, 12 H), 1.21 (s, 6 H), 2.42 (br s, 2 H), 3.26 (m, 2 H); mass spectrum (70 ev), *m/e* (relative intensity) 171 (1), 168 (16), 155 (10), 153 (36), 150 (25), 137 (56), 135 (97), 125 (36), 83 (100).

1-Hydroxy-α,α,3,3,5,5-hexamethyl-1-cyclohexanemethanol (18): IR (CCl_4) 3460, 2865, 1450, 1375, 1360 cm^{-1}; NMR ($CDCl_3$) δ 0.91 (s, 6 H), 1.23 (s, 12 H), 1.36–1.47 (complex), 1.69 (br s, 1 H); mass spectrum (70 eV), *m/e* (relative intensity) 196 (1), 181 (11), 178 (14), 163 (42), 155 (100), 137 (60), 121 (41), 107 (42), 97 (85), 83 (61).

Registry No.—1, 1197-66-6; 2, 826-36-8; 3, 22842-41-7; 4, 14376-79-5; 5, 64113-64-0; 6, 20931-50-4; 7, 64113-65-1; 8, 64113-66-2; 9, 55196-74-2; 10, 2403-88-5; 11, 64113-67-3; 12, 20931-54-8; 13, 64113-68-4; 14, 64113-69-5; 15, 64113-70-8; 16, 64113-71-9; 17, 2650-40-0; 18, 64113-72-0; 2,6-dimethyl-2,5-heptadien-4-one, 504-20-1.

Supplementary Material Available: Mass spectra of compounds 5, 9, and 15 (3 pages). Ordering information is given on any current masthead page.

References and Notes

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