

Photochemistry of 4-Methylverbenene

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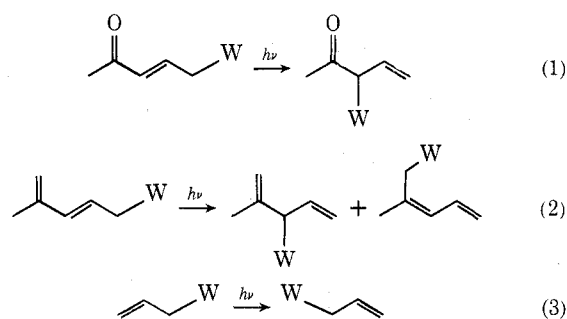
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Received March 26, 1974

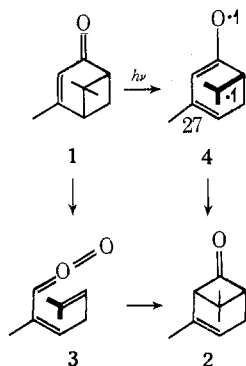
The photochemistry of 4-methylverbenene (11) has been investigated. Both sensitized and direct irradiation of 11 leads to production of 3-methylenelimonene (12). The mechanism of this process and comparison of the excited-state reactivity of 11 with that of structural and chromophoric analogs are discussed.

The photochemistry of compounds which possess the capability of reacting by [1,*n*]-sigmatropic pathways has received modest attention since the early discovery by Hurst and Whitham¹ of the conversion of verbenone (1) to chrysanthenone (2). In recent years, several excited-state isomerization reactions of this type have been uncovered.²

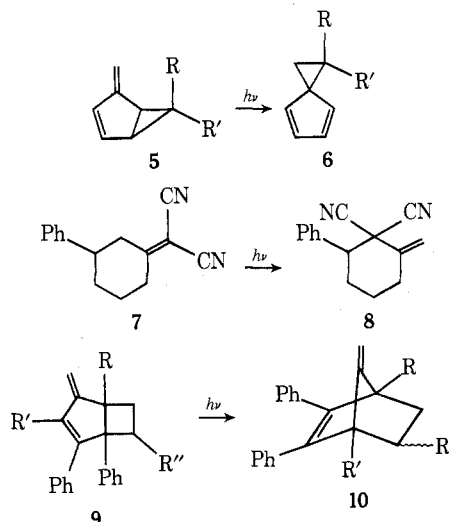
These transformations appear to be part of a general class of reactions in which compounds possessing conjugated-enone and -diene and monoolefin chromophores with substituted alkyl moieties α to the π group rearrange to products having the alkyl substituents 1,3- or 1,5-relocated. In general, the reactions result in the conversion of conjugated enones to β,γ -unsaturated ketones, of 1,3-dienes to 1,4-dienes or rearranged 1,3-dienes, and of monoolefins to their regioisomers, as depicted in a schematic way in eq 1-3.



However, mechanistic dissimilarities between the reactions appear to preclude their inclusion into one class. Although in a formal sense each transformation could be depicted as a simple 1,3- or 1,5-sigmatropic carbon migration, the evidence suggests that the actual mechanism for isomerization in each case is dependent upon the structure and chromophore within the reactant and the excited-state multiplicity utilized for reaction. Of particular interest are the observations made on the verbenone to chrysanthenone rearrangement. Two competing mechanisms appear to operate, one involving a nonconcerted 1,3-alkyl shift and the other a retro-cycloaddition to the ketene 3 followed by readdition.⁶ Both pathways are followed in reaction of triplet excited verbenone⁷ and, thus, most probably pass through the triplet diradical 4.



On the other hand, the stereochemical courses of singlet reactions of the related 3-methylenebicyclo[3.1.0]hexene 5⁹ and olefin 7¹⁰ suggest mechanisms having two consecutive 1,2-carbon shifts or a concerted 1,3-migration, respectively. Evidence which suggests that the chromophore, *i.e.*, enone *vs.* diene or monoolefin, contained within the reacting system is not solely influential in determining reaction mechanisms is found in the study of the 3-methylenebicyclo[3.2.0]heptenes 9.¹¹ Nonconcerted mechanisms in these cases are proposed to account for the absence of stereospecificity in rearrangement.



Thus, with these observations in mind, we have prepared 4-methylverbenene (11, 4-methylene- α -pinene) in order to investigate the photochemistry of a noncarbonyl π analog of verbenone. We now would like to report our results from this study which indicate a departure from the photochemical behavior observed for related systems.

Results

The direct and sensitized photochemistry of 4-methylverbenene (11),¹² prepared by the reaction of verbenone⁶ with methylenetriphenylphosphorane, was investigated in order to determine the nature of the preferred excited state reaction pathways.

Triplet Sensitized Irradiation. Irradiation of a pentane solution of 11 (1.2×10^{-2} M), containing benzophenone (0.1 M) as a triplet sensitizer,¹⁴ afforded two products, separable from the starting diene and benzophenone by alumina chromatography and glc. The ratio of the two photoproducts was found to be dependent upon the extent of conversion of 11, the minor product being nearly absent at low conversions (*vide infra*). Thus, 4-methylverbenene triplet reacts cleanly to yield only one product. This photoproduct is isomeric with 4-methylverbenene and its proton nmr spectrum is uncharacteristically simple, having 5 vinyl and 11 allylic and methylene protons. Its ultraviolet spectrum (λ_{\max} 236 nm), which is quite similar to that of 11, in-

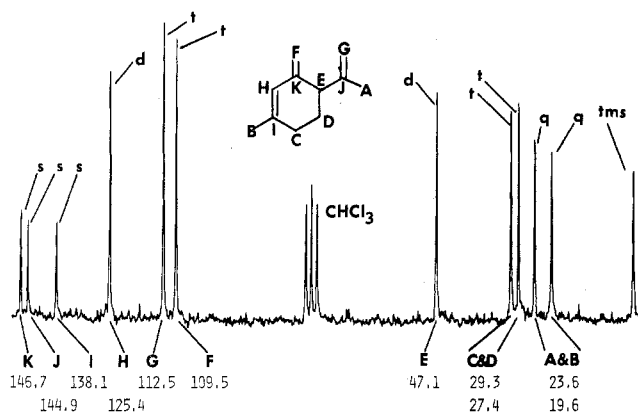
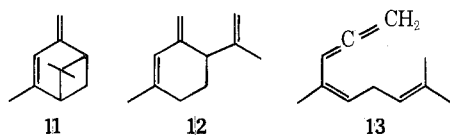


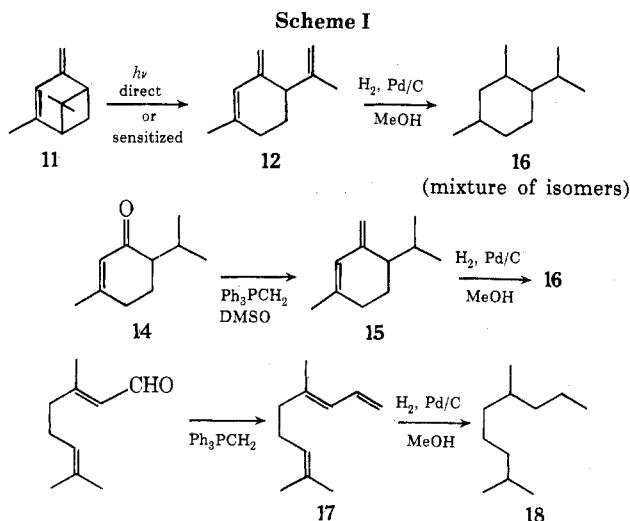
Figure 1. Carbon-13 nmr spectra of 3-methylenelimonene. Chemical shifts are recorded in parts per million relative to tetramethylsilane. The undecoupled spectra derived carbon-proton multiplicities are given along with the carbon assignments.

indicates that the photoproduct contains either a heteroannular conjugated-diene chromophore with one alkyl substituent or a trisubstituted acyclic diene chromophore. Likewise the mass spectrum of the material is nearly identical with that of 4-methylverbenene; both have a molecular ion at m/e 148, a base peak at m/e 133 ($P - 15$), and an intense m/e peak corresponding to the loss of an uncharged isopropyl group.

On the basis of this data and the known photochemistry of α -pinene¹⁵ and verbenone, chromophoric and structural analogs of 11, two structures emerged as likely candidates for the sensitized photoproduct; these were 3-methylenelimonene (12) and 4,8-dimethyl-1,2,4,7-nonatetraene (13).



Further spectral and chemical data allowed the unambiguous assignment of 12 as the sole triplet photoproduct of 4-methylverbenene. First, the infrared spectrum of this material does not contain the characteristic band for a vinyl allene chromophore near the 1950-cm^{-1} region as would have been expected for 13.^{16,17} More firm support for 12 derives from the hydrogenation and independent synthetic results summarized in Scheme I. Exhaustive cat-



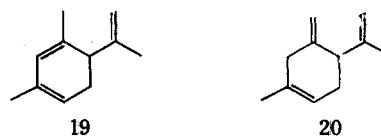
alytic hydrogenation of the photoproduct leads to three gas chromatographically separable products, having molecular

weights (by mass spectrum, parent at m/e 154, *vide infra*) that indicate the consumption of 3 mol of hydrogen in the production of each. The nature and relative quantities of the three hydrogenation products are insensitive to reaction time, and thus the hydrogenation appears complete. Therefore the photoproduct must be a monocyclic triene as is 12.

Definitive proof of the hydrogenation product structures derives from their independent synthesis from piperitone (14). The sequence involves reaction of 14 with methylenetriphenylphosphorane, yielding the methylenedihydroterpinene 15, followed by exhaustive hydrogenation. The gas chromatographic retention times of the synthesized and photoproduct-derived hydrogenation products are identical. The mass spectra of materials from both sources are nearly identical and characteristic of the 1,3-dimethyl-6-isopropylcyclohexanes 16.¹⁸

To remove all questions concerning allene 13 as the possible structure for the triplet photoproduct, 2,6-dimethylnonane (18)¹⁹ was prepared from citral *via* the triene 17²⁰ (see Scheme I). The chromatographic behavior and mass spectrum of 2,6-dimethylnonane were found not to match those of any of the three photoproduct-derived hydrogenation products.

The results summarized above are consistent with the assignment of 3-methylenelimonene (12) as the product from the sensitized photolysis of 11. Owing to its import in the mechanistic interpretation of the photoreaction observed, it was necessary to obtain more firm support for the location of the unsaturation present in the photoproduct skeleton, *i.e.*, to obtain further evidence beyond the nmr and uv spectral data presented above to eliminate the cyclohexadiene 19 and methylenecyclohexene 20. The C-13



nmr spectrum of the photoproduct is displayed in Figure 1. As expected on the basis of structure 12, the spectrum contains two methyl and two saturated methylene resonances in the regions predicted from inspection of spectra of model systems, in particular that of 1-methyl-4-isopropyl-3-methylenecyclohexane (15). Exceptionally characteristic are the quaternary vinyl carbon resonances at 146.7 and 138.1 ppm (singlets in the undecoupled spectrum) due to carbons K and I, the vinyl methine at 125.4 ppm for carbon H, and the vinyl methylene at 109.5 ppm for carbon F, when compared to the corresponding respective carbon resonances in the model 15, at 146.4, 137.7, 124.9, and 109.1 ppm. These data well confirm the structure of 12 and together with the other spectral properties rule out 19 and 20.

Direct Irradiation. Direct irradiation of a degassed pentane solution of 4-methylverbenene ($2.6 \times 10^{-2} M$), using Vycor filtered light, led to production of a complex photomixture containing unreacted 11 and one major product, along with several minor unidentified photoproducts. The major product obtained under these conditions was determined to be 3-methylenelimonene (12) on the basis of the equivalence of its spectral and physical parameters with those of material derived from the sensitized photolysis.

Varying Conversion Photolysis. Indirect, but sufficient, proof that the minor photoproduct of the sensitized photolysis originates from a secondary photochemical reaction of the initially formed 3-methylenelimonene comes from varying conversion sensitized runs, the results of which are summarized in Figure 2. Thus, at low conversions

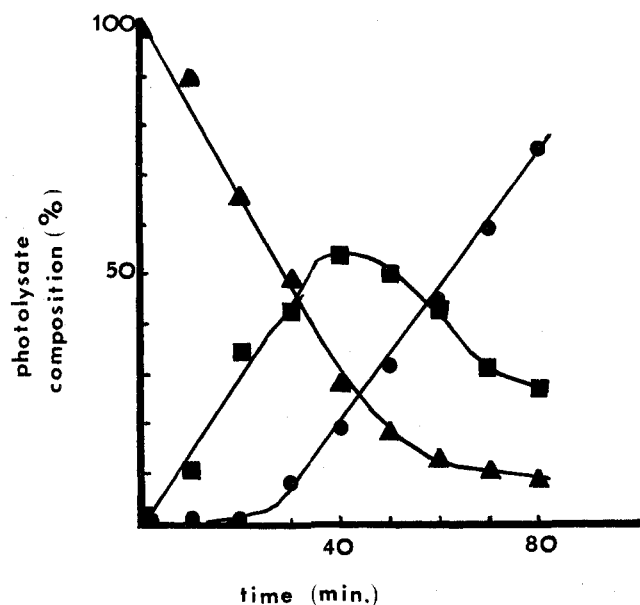


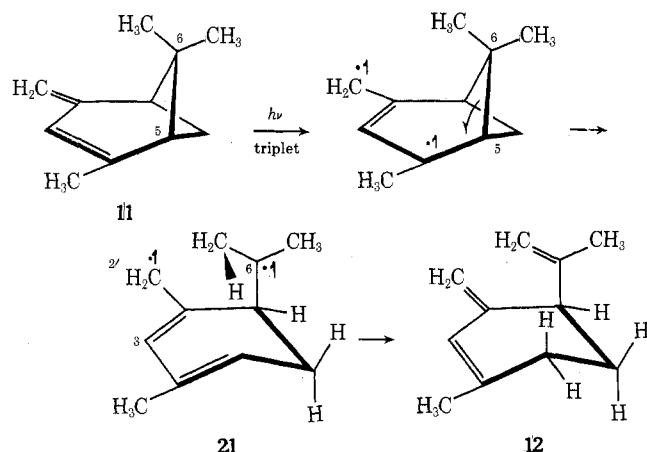
Figure 2. Plot of photolysate composition in benzophenone-sensitized run. The relative percentages of starting 4-methylverbenene (\blacktriangle), 3-methylenelimonene (\blacksquare), and the unidentified secondary product (\bullet) are recorded vs. the time of irradiation.

12 is the sole photoproduct detected; its yield diminishes simultaneously with build-up of the minor photoproduct.

Discussion

The photochemical rearrangement of 4-methylverbenene (11) to 3-methylenelimonene (12) represents a novel departure from reaction pathways followed by closely related structural and chromophoric analogs, like verbenone (1).¹⁻⁶ A plausible mechanism for this unusual, but easily rationalizable, photoisomerization involves a simple nonconcerted process, having as its initial step rupture of the high-energy C-5-C-6 bond with concomitant formation of the highly stabilized diradical 21. Ensuating transformation of 21 to 3-methylenelimonene (12) proceeds *via* an intramolecular disproportionation having transfer of one of the C-6 methyl hydrogens to C-5 of the pentadienyl radical moiety.

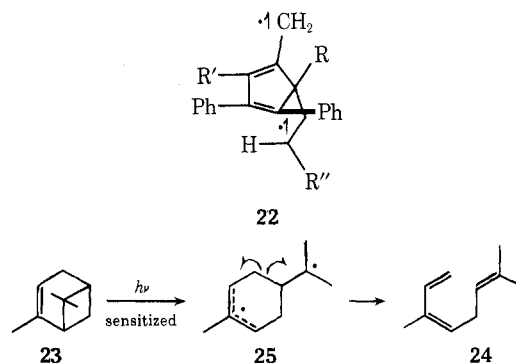
Three important features of the 4-methylverbenene isomerization and its likely mechanism warrant further brief comment. First, the preferred triplet reaction pathway followed by 11 is quite different from those employed in triplet rearrangements of closely related compounds. For example, and in contrast, the familiar verbenone to chrysantheone transformation has been postulated to involve two mechanistically distinct pathways, both of which pass



through the initially formed diradical 4, one having ensuing bonding between C-6 and C-3 and the other further collapse to the ketene 3 followed by ground-state cycloaddition (*vide supra*).⁶ Indirect support for the diradical nature of one of the two modes utilized by excited verbenone derives from the stereochemical results of Cargill and coworkers³ from studies of related bicyclic ketones. Loss of stereochemical integrity about the migrating carbon in this case has been logically interpreted in terms of a nonconcerted mechanism. The implication is that the 1,3 carbon shift in the verbenone isomerization follows similar pathways.

In addition, Schuster⁸ has shown that rearrangement to chrysantheone is a triplet reaction of verbenone and has thus concluded that a nonsynchronous mechanism is likely.

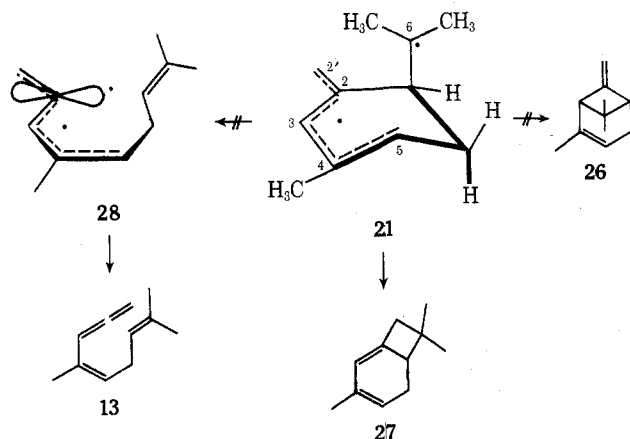
Olefin analogs appear to utilize similar reaction pathways for rearrangement. One of the more characteristic examples is found in the triplet sensitized isomerization of the 3-methylenebicyclodiene 9 to a mixture of 5-endo- and -exo-substituted 7-methylenenorbornenes 10a and 10b.¹¹ Here, as in Cargill's example, the nonstereospecific nature of the rearrangement could be interpreted in terms of a stepwise mechanism *via* the long-lived diradical intermediate 22. The interesting sensitized conversion of α -pinene (23) to *cis*-ocimene (24)¹⁵ represents another case in which triplet reaction of a structural analog of 11 appears to rearrange through a diradical resulting from cleavage of the σ bond in conjugation with the excited chromophore. In this example, the diradical, 25, adopts, preferentially, the familiar cleavage route for further reaction. This pathway is characteristic of those followed by 1,4-diradicals produced in other ways.²¹



It is significant that the triplet conversion of 4-methylverbenene to 3-methylenelimonene is still another example which implicates the intermediacy of initially formed diradicals in rearrangements of systems like those found in eq 1-3 above. In this case, the "diradical detector" is not present as a stereochemical marker, but rather in the familiar disproportionation reaction which hindered free radicals easily and characteristically undergo.²²

Thus, the major difference between triplet reaction of 11 and those of its carbonyl and olefin analogs appears to result solely from the nature of preferred, low-energy reaction pathways followed by the generated diradical intermediate. The differences and the exclusive adherence to the internal disproportionation route by 11, however, remain perplexing. The apparent exclusion of alternate reaction modes from the diradical 21, such as C-3-C-6 bonding leading to 6-methylenechrysantheone (26, C-2'-C-6 bonding to the bicyclooctadiene 27, and C-1-C-2 bond cleavage yielding the divinylallene 13, may perhaps reflect the odd-electron spin density at the various positions in the pentadienyl radical moiety²³ (weighted at the termini more heavily than at the central atom) and the initially formed conformer of 21, having the C-6 grouping pseudo-axially disposed

and thus in closer proximity to C-5 than to C-2'. Recombination between C-6 and C-5 would lead to regeneration of the starting verbenene while disproportionation involving the C-5 center results in the production of **12**.²⁵ Divinylallene **13** production, by a pathway analogous to that followed in the α -pinene to *cis*-ocimene conversion, would require collapse of diradical **21** to the initially nonstabilized diradical **28**, which contains the odd electron at C-2 in an orbital perpendicular to the π system.



In conclusion, 4-methylverbenene undergoes a rather unusual triplet reaction which is both specific and deviant from that expected on the basis of the known photochemistry of closely related structural and chromophoric analogs.

Experimental Section

General. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were recorded on Varian T-60 or HA-100 (proton) and Jeol PS-100 (carbon) spectrometers with tetramethylsilane as the internal standard. Infrared spectra were taken with a Perkin-Elmer 237 spectrophotometer and ultraviolet spectra were measured using a Beckman Acta-III spectrophotometer. Gas chromatographic separations were conducted using a Varian Model 2700 chromatograph and analyses using a Varian Model 940 chromatograph. Mass spectra were obtained using a Varian MAT CH-7 with a gc inlet and a CEC-21-110 mass spectrometer.

4-Methylverbenene (11). An ethereal solution containing 0.067 mol of *n*-butyllithium was added dropwise to a solution of 27.0 g (0.067 mol) of triphenylphosphonium iodide in 120 ml of dimethyl sulfoxide. The resulting mixture was stirred at 20° for 0.5 hr and then heated to reflux while a solution of 7.2 g (0.05 mol) of verbenene in 25 ml of dimethyl sulfoxide was added. After stirring overnight at reflux, the solution was cooled, quenched with water, and extracted with ether. The combined ethereal extracts were dried and concentrated by careful distillation. The precipitated triphenylphosphine oxide was removed from the pot residue by filtration and the filtrate was fractionally distilled, yielding 2.43 g (28.3%) of 4-methylverbenene, bp 45° (3.5 mm) [lit.¹³ bp 60° (15 mm)]. The spectral properties of this compound were identical with those reported previously.¹³

Photolyses of 4-Methylverbenene. Sensitized Irradiation. A nitrogen-purged solution of 4-methylverbenene (4.0 mM) and benzophenone (126 mM) in pentane was irradiated for 10 min using an apparatus consisting of a Hanovia 450-W medium-pressure lamp in a water-cooled quartz immersion well with a Pyrex glass filter. The photolysate was concentrated carefully to a volume of 50 ml, percolated with pentane through an alumina column (10 × 2 in., Matheson chromatographic grade, 923 80–200 mesh), and concentrated carefully again. Glc analysis (10 ft × 0.25 in. column, packed with 4% SE-30 on ABS Anakromb, 120°, 120 ml/min) indicated the presence of the following: unreacted 4-methylverbenene (69.2%), a major photoproduct (11.8%), and a high-boiling material (19%). The major photoproduct, later identified as 3-methylenelimonene (**12**), was isolated by preparative glc (retention time 13 min, using the same conditions) as a clear liquid having the following spectral properties: proton nmr (CCl₄) δ 1.8 (br s, 6 H, methyls), 2.1 (m, 5 H, methylenes and methine), 4.8 (m, 4 H, vinyl methylenes), 5.9 (s, 1 H, vinyl); carbon-13 nmr, see Figure 1; ir (liq-

uid film) 6.1, 6.25, 7.0, 7.3, and 11.4 μ ; uv (acetonitrile) 236 nm (ϵ 14,200); mass spectrum *m/e* (rel intensity based upon base peak at *m/e* 133) 148 (47), 133 (100), 105 (51), 91 (55), 28 (66).

Anal. Calcd for C₁₁H₁₆: C, 89.19; H, 10.81. Found: C, 89.33; H, 10.96.

Varying Conversion Sensitized Photolyses. A nitrogen-purged solution of 4-methylverbenene (15.6 mM) and benzophenone (31.5 mM) in pentane was used employing the immersion apparatus described above. At 10-min intervals, 2-ml aliquots were removed from the photolysis mixture and analyzed by glc (10 ft × 0.125 in., 1.5% OV-101 on 100/20 Varoport 30, 60°, 13 ml/min flow rate). The data obtained are plotted in Figure 2.

Direct Irradiation. Direct irradiations of 4-methylverbenene were conducted on 26 mM, degassed and nitrogen purged, pentane solutions in sealed quartz tubes mounted adjacent to the quartz immersion well containing a Vycor glass filter. The solutions were irradiated for 0.75 hr. The photolysate, after removal from the tubes, was concentrated by careful distillation and analyzed by glc using the conditions described above. A typical photolysis yielded a photolysate containing unreacted 4-methylverbenene (27.5%), and the identical major (20.4%) and many minor photoproducts as obtained in the sensitized reaction.

Hydrogenation of the Major Photoproduct. Hydrogenation of 40 mg of the major photoproduct, derived from both the direct and sensitized photolyses, was conducted by bubbling hydrogen through a suspension of pre-hydrogen-saturated 5% palladium on charcoal (5 mg) and the photoproduct in 5.0 ml of absolute methanol for 8 hr. The solution was filtered and analyzed by glc (10 ft × 0.125 in., 1.5% OV-101 on 100/20 Varoport 30, 60°, 13 ml/min flow rate). Three components with retention times of 3, 6, and 7 min were detected. The gc-mass spectral analyses indicated that they were isomeric and corresponded to products resulting from the absorption of 3 mol of hydrogen. Later comparison of the mass spectra of the hydrogenation products with those of independently synthesized material showed that they are the isomeric 1-isopropyl-2,4-dimethylcyclohexanes.

To ensure that catalyzed isomerization of the photoproduct had not occurred during the course of the hydrogenation, a solution of the catalyst and photoproduct in methanol was stirred in the absence of hydrogen for 8 hr. Glc analysis of the filtered solution showed that only nonisomerized photoproduct remained.

2,6-Dimethylnonane. Hydrogenation of 4,8-dimethyl-1,3,7-nonatriene¹⁹ prepared by the Wittig reaction of methylenetriphenylphosphorane with citral, was carried out, using 5% palladium on charcoal in absolute methanol, as described above. Glc analysis of the product mixture showed one component (retention time 6 min on 10 ft × 0.125 in., 1.5% OV-101 on 100/20 Varoport 30, 60°, 13 ml/min flow rate) identified as 2,6-dimethylnonane.¹⁹ The mass spectral fragmentation pattern of this compound was as follows: *m/e* (rel intensity based upon base peak at *m/e* 71) 156 (2), 141 (3), 71 (100), 70 (65), 57 (93), 56 (34), and 55 (46).

1-Methyl-4-isopropyl-3-methylenecyclohexene. To a solution of methylenetriphenylphosphorane, prepared from 65 mmol of *n*-butyllithium and 26.5 g (65 mmol) of methyltriphenylphosphoniumiodide in 200 ml of dimethyl sulfoxide, was added 5.0 g (32 mmol) of piperitone (K and K Laboratories) in 10 ml of dimethyl sulfoxide. The resulting solution was refluxed for 12 hr, cooled, quenched with water, and extracted with pentane. The combined pentane extracts were dried, concentrated to 25 ml by fractional distillation, and percolated with pentane through an alumina column (10 ft × 2 in., Matheson chromatographic grade 923, 80–200 mesh). The pentane was again removed by distillation and the pot residue was further purified by preparative glc (10 ft × 0.25 in., 4% SE-30 on ABS Anakromb, 120°, 90°, 100 ml/min flow rate). The compound having a 20-min retention time was shown to be 1-methyl-4-isopropyl-3-methylenecyclohexene (0.3 g, 6%) on the basis of the following spectral properties: proton nmr (CDCl₃) δ 1.0 (d, 6 H, methyls), 1.8 (br s, 3 H, vinyl methyl), 2.1 (m, 6 H, saturated CH and CH₂'s), 4.7 (d, 2 H, vinyl methylenes), 5.9 (s, 1 H, vinyl); uv (acetonitrile) 236 nm (ϵ 15,200); ir 6.15, 6.3, 7.3, 7.4, 11.5 μ .

Anal. Calcd for C₁₁H₁₈: C, 87.93; H, 12.07. Found: C, 87.87; H, 11.91.

Isomeric 1-Isopropyl-2,4-dimethylcyclohexanes. Hydrogenation of 40 mg (0.27 mmol) of 1-methyl-4-isopropyl-3-methylenecyclohexene in 10 ml of absolute methanol containing 5 mg of 5% palladium on charcoal was carried out by bubbling hydrogen through the suspension for 2 hr. The solution was filtered and analyzed by glc (same conditions as above). Three components of re-

tention times 6, 8, and 10 min were detected. Gc-mass spectral analysis of the first component showed that it was identical with the hydrogenated photoproducts. The other two components were identified as products of partial hydrogenation.

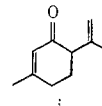
Acknowledgment. Grateful acknowledgment is made to the Robert A. Welch Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Environmental Quality Program of Texas A&M University for generous support of this research. The authors would like to express their appreciation to Dr. Robert Stipanovic for many helpful discussions and for recording the gc-mass spectra.

Registry No.—1, 80-57-9; 11, 51911-75-2; 12, 51911-77-4; 14, 89-81-6; 15, 51911-80-9; 16, 51911-81-0; 17, 51911-82-1; 18, 17302-28-2.

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- quantities of isopiperitenone (**i**) formed on photolysis of verbenone⁶ probably results from disproportionation of the intermediate diradical **4** by pathway analogous to the production of **12**.
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Oxazolines. IX. Synthesis of Homologated Acetic Acids and Esters

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Received April 16, 1974

The lithio salt of 2,4,4-trimethyl-2-oxazoline (**1a**) reacts with alkyl halides affording the 2-alkyloxazolines **3** which may be hydrolyzed to homologated acetic acids. Dialkylation leads to α,α -dialkylacetic acids **5**. Alternatively, the alkylated oxazolines may be directly transformed into esters derived from the use of an appropriate alcoholic solvent. The lithio oxazolines also add smoothly to carbonyl compounds producing, after hydrolysis, α,β -unsaturated acids (**25**) or esters (**26**). Under certain conditions, the formation of β -hydroxy esters (**27**) is allowed, thus providing a convenient alternative to the Reformatsky reaction. The scope and limitations of this novel approach to alkylated acetic acids are also described.

The recent surge of techniques developed for homologation of acetic acids has advanced synthetic methodology considerably. When one recalls that the only generally useful routes available prior to 1967 were the classical malonic and acetoacetic ester syntheses, these new methods involving alkali metalated acetic acids and esters,^{3,5,6,8} organo-copper derivatives,⁷ and organoboranes⁴ have all demonstrated that they are more versatile or superior in many respects. Thus, electrophiles may now be directly introduced onto $-\text{CH}_2\text{CO}_2\text{R}(\text{H})$ or $\text{RCHCO}_2\text{R}(\text{H})$ affording alkylated or dialkylated acetic acids or esters.

In 1970 a preliminary account appeared^{9a} which described the potential utility of the simple 2-oxazoline **1** as a precursor to homologated acetic acids and esters. A more complete description of this method and its scope is now presented. Furthermore, the oxazoline precursor may also provide a useful alternative to the Reformatsky reaction

(β -hydroxy esters) and, as described in the accompanying paper,^{9b} to a variety of butyrolactones.

The requisite 2-oxazolines (**1**) are readily prepared by treating 2-amino-2-methyl-1-propanol with carboxylic acids and removal of the heterocycle by distillation.¹⁰ An alternative technique involves the condensation of acids, acid chlorides, or esters with 2,2-dimethylaziridine followed by rearrangement.^{11,12} The latter method leads to the iso-

