Direct Oxidation of Durene to a Cyclohexadienone. Chemistry and Photolysis[1]

HAROLD HART AND RICHARD M. LANGE[2]

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823

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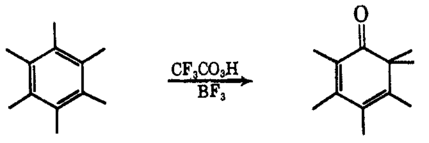
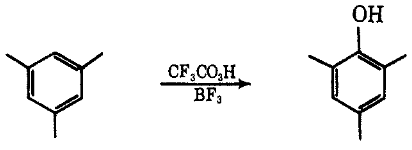
The major oxidation product of durene with peroxytrifluoracetic acid–boron fluoride in methylene chloride, or with 90% hydrogen peroxide in acetic–sulfuric acid was 3,4,6,6-tetramethyl-2,4-cyclohexadienone (V), which could be obtained in yields over 75%. Duroquinone, durohydroquinone, and durophenol were among the minor oxidation products. The dienone gave a Diels–Alder adduct with maleic anhydride, and was readily converted to the cross-conjugated 6-methylene-1,4-cyclohexadienes (XVIII and XXI) by 1,2 addition of methyl Grignard, or reduction with lithium aluminum hydride, followed by 1,4 dehydration of the resulting alcohols. Dienone (V) was recovered from prolonged irradiation (Pyrex) in moist or anhydrous ether, but in ethanol it rapidly photolyzed with ring opening, giving ethyl 3,4,6-trimethylhepta-3,5-dienoate (XXV) in excellent yield. The presence or absence of certain methyl groups in 2,4-cyclohexadienones can completely alter their photochemical behavior.

Oxidation of hexaalkylbenzenes with electrophilic oxidants such as peroxytrifluoroacetic acid–boron fluoride or hydrogen peroxide in strong acid has been shown to proceed with Wagner–Meerwein rearrangement, giving hexaalkylcyclohexadienones in good yield. Thus hexamethylbenzene (I) is converted to hexamethyl-2,4-cyclohexadienone (II) at 0° in about 90% yield.[1,3] Less substituted benzenes under similar conditions give phenols instead, by electrophilic attack at an unsubstituted ring position. For example, mesitylene (III) is converted to mesitol (IV) in nearly quantitative yield.[4]



I II



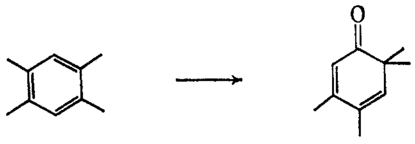
III IV

The two tetramethylbenzenes studied thus far showed different behaviors on oxidation. Isodurene, like mesitylene, gave a good yield of the corresponding phenol,[4] whereas prehnitene afforded a rather complex mixture of products, including not only the expected phenol, but rearranged phenols and even a small yield of a cyclohexadienone.[4] It seemed desirable to examine the remaining tetramethylbenzene, durene, and this paper reports the results of its oxidation with two electrophilic oxidants, peroxytrifluoro acetic acid and acidic hydrogen peroxide. Also included are some interesting ground-state chemistry and photochemistry of the major oxidation product, 3,4,6,6-tetramethyl-2,4-cyclohexadienone.

Results and Discussion

Durene Oxidation.—Durene was oxidized at 5–8° with peroxytrifluoracetic acid in methylene chloride. Boron fluoride was passed through the reaction mixture or added in the form of its etherate, at a molar rate equal to that of the oxidant. In general, the oxidant was used in 10% molar excess over the durene, but this was not critical, since substantially the same yields of products were obtained when a twofold excess of durene was used. Reaction was essentially complete on mixing the reactants.

The major product was 3,4,6,6-tetramethyl-2,4-cyclohexadienone (V), obtained in yields as high as 78%, based on converted durene (conversions ranged from about 65 to 80%). The structure of V follows from its analysis, spectral properties, and chemical transformations. The infrared spectrum of V showed conjugated carbonyl and double bonds (1656 and 1640 cm^{-1}) and a *gem*-dimethyl group (1393 and 1380 cm^{-1}). The ultraviolet spectrum has a single $\lambda_{\max}^{\mathrm{EtOH}}$ at 316 mμ (log ϵ 3.36), close to that predicted by Woodward's rules[5] for a 3,4-dialkyl homoannular conjugated cyclohexadienone (314 mμ); the extinction coefficient is also reasonable.[1,3] The nmr spectrum of V had a six-proton singlet at τ 8.92 (*gem*-dimethyl group), and two three-proton doublets at 8.08 and 7.97 (J = 1.5 cps, allylic methyls each split by neighboring vinyl protons). The lower field allylic methyl is due to the methyl group at C-3, since treatment of V with excess 10% $NaOCH_3$ in CH_3OD caused the peak at τ 7.97 to disappear; exchanges at this position are particularly facile.[1] The vinyl protons of V appeared as multiplets at τ 4.27 and 4.10.



V

There are in fact six possible *x*,*x*,6,6-tetramethyl-2,4-cyclohexadienones (V–X). The evidence presented thus far tends to rule out all but V, VII, and X (only these have exchangeable methyls at C-3), although it is possible that the methyl at C-5 might be exchangeable in some of these.[6] Of these, X is unlikely because

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[1] Paper VI in a series on oxidations with peroxytrifluoracetic acid–boron fluoride. For paper V, see H. Hart, P. M. Collins, and A. I. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

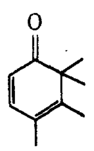
[2] National Science Foundation Postdoctoral Fellow, 1964–1965. We also gratefully acknowledge grant support from the National Science Foundation.

[3] A. I. Waring and H. Hart, *J. Am. Chem. Soc.*, **86**, 1454 (1964).

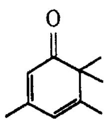
[4] C. A. Buehler and H. Hart, *ibid.*, **85**, 2177 (1963); H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2397 (1964).

[5] H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 219.

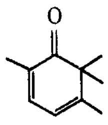
[6] Exchange at C-5 is orders of magnitude slower than at C-3 in hexamethyl-2,4-cyclohexadienone; see ref 1.



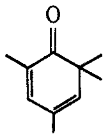
VI



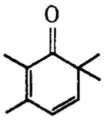
VII



VIII



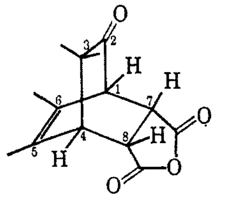
IX



X

of the nmr spectrum, since the vinyl protons would appear as an AB quartet, and the allylic methyls would not be equally coupled with them. A decision between V and VII cannot be made from the spectroscopic data alone.

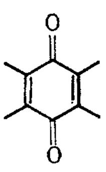
A clear-cut decision in favor of V, which unequivocally eliminates *all* the other possibilities, can be made by examining a Diels–Alder adduct of the dienone. Only V should show two allylic methyl groups in a Diels–Alder adduct. On refluxing with maleic anhydride in benzene, the dienone from durene afforded a white, crystalline adduct, mp 113–114°, which had an nmr spectrum consistent with structure XI. Two doublets



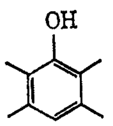
XI

(three protons each, $J = 1.0$ cps) at τ 8.15 and 8.10 correspond to the two allylic methyl groups, fixing the positions of the methyls at C-3 and C-4 in the original dienone (structure V).

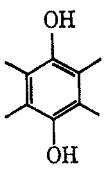
Other products of the durene oxidation, each formed in relatively small yield, included duroquinone (XII) durophenol (XIII), tetramethylhydroquinone (XIV), and a trace of 2,3,4,5-tetramethylphenol. These were identified by comparison of infrared spectra and vpc retention times with those of authentic samples.



XII



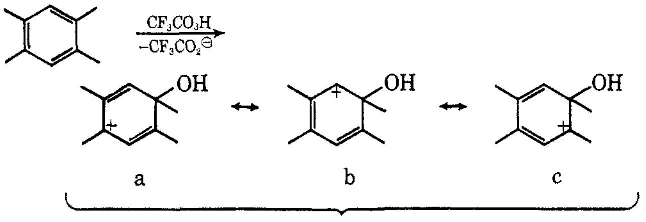
XIII



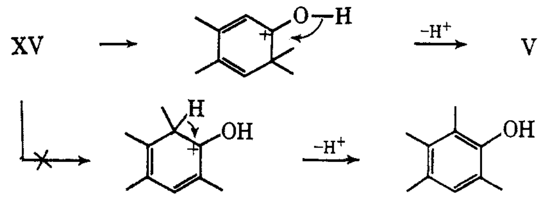
XIV

The oxidation of durene was also attempted with 90% hydrogen peroxide in a mixture of acetic and sulfuric acids. This oxidant had been effective[1] in oxidizing hexamethylbenzene to the corresponding dienone (II). At 25° durene was about 50% converted to oxidation products in 1.25 hr. The yield of dienone dropped, however, to 52%, and duroquinone was formed in considerably greater amounts (35%, *cf.* about 4% with peroxytrifluoracetic acid).

Mechanism of the Oxidation.—Although the exact nature of the attacking species is as yet unsettled, strong evidence has been presented supporting the intermediacy of an electrophilic, cationic reactant.[7] The minor oxidation products XII–XIV are readily accounted for by electrophilic attack of peroxytrifluoracetic acid on durene at an unsubstituted ring position. The dienone (V) is presumably formed by similar attack at a methyl-bearing carbon, leading to the intermediate carbonium ion XV. Of the contributors to this resonance hybrid, presumably c is more important than b, since methyl migration occurs in the direction expected from c; *i.e.*, the product is V. It is perhaps surprising that no product corresponding to methyl migration in the alternative direction [*i.e.*, isodurenol (XVI)] is produced.



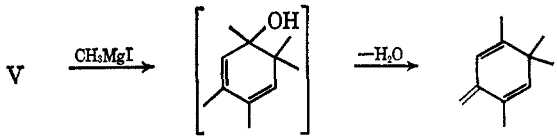
XV



XVI

It is also necessary to rationalize why the oxidant preferentially attacks a methyl-substituted carbon. Two factors may contribute. First, the intermediate pentadienyl cation is stabilized by an *o*- and a *p*-methyl if attack occurs at a substituted carbon, whereas it is stabilized by two *o*-methyls if oxidation occurs at an unsubstituted carbon. *p*-Methyls may be more effective than *o*-methyls. Second, the already substituted position is flanked by only one methyl group, whereas the unsubstituted position is flanked by two methyls; thus a steric factor may be involved. Admittedly, both of these rationalizations are weak, but they are the only ones to fall upon at the moment. Regardless of the mechanism, the oxidation makes the otherwise difficultly accessible dienone V readily available.

Reactions of V.—When V was treated with methylmagnesium iodide and worked up with ammonium chloride, the triene 1,3,3,4-tetramethyl-6-methylenecyclohexa-1,4-diene (XVIII) was obtained. The intermediate alcohol (XVII) was not isolated. The structure of XVIII rests largely on spectroscopic data. The infrared spectrum shows a terminal methylene (885 cm^{-1}). The ultraviolet spectrum had a λ_{max}^{EtOH} 248 mμ (log ϵ 3.63), which compares favorably with related compounds with one or two more methyl groups.[1] This spectrum, more than any other single piece of evidence, eliminates the alternative structure XIX, which should absorb at about 308 mμ.[8] The



XVII XVIII

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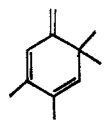
[7] A. I. Davidson and R. O. C. Norman, *J. Chem. Soc.*, 5404 (1964), and references cited therein.

[8] See ref 5, p 200.

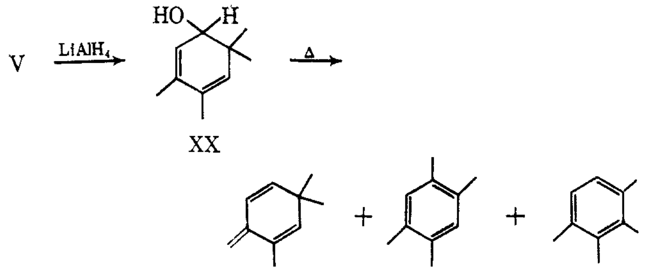


XIX

nmr spectrum of XVIII is consistent with the assigned structure (see the Experimental Section). This affords another example of the preference for formation of cross-conjugated, rather than completely conjugated trienes in this type of system, as was previously noted.[1]

A second product of the Grignard addition was pentamethylbenzene, formed by acid-catalyzed rearrangement of XVII or XVIII.

Lithium aluminum hydride reduction of V gave the dienol XX in 91% yield. This was dehydrated in the injector block (160°) of a gas chromatograph to 1,3,3-



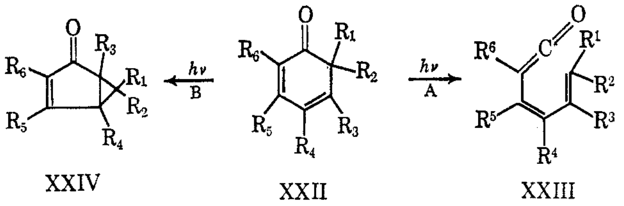
XX

XXI

trimethyl-6-methylenecyclohexa-1,4-diene (XXI) in 79% yield, with durene (14%) and prehnitene (7%) as minor products. Treatment of XX in carbon tetrachloride with hydrochloric acid gave the same dehydration products in 44, 29, and 27% yields, respectively. The structure of XXI follows from its spectra. Infrared showed a terminal methylene (878 cm^{-1}); the ultraviolet spectrum had maxima at 247 mμ (log ε 3.84) and 221 mμ (log ε 3.16).

A reasonably complete nmr assignment was possible, which is consistent with the structure (see Experimental Section).

Photolysis of V.—Most 2,4-cyclohexadienones studied so far undergo ring opening on photolysis in Pyrex, to give a diene–ketene (XXIII),[9,10] although this reaction (path A) may encounter some difficulty, particularly if R_4 = alkyl. For example, XXII (R_1 = allyl, $R_2 = R_4 = R_6$ = methyl, $R_3 = R_5$ = H) gave no photolysis product after 93 hr in moist ether,[9] although amide derived from XXIII could be obtained if cyclohexylamine was present. The difficulty has been ascribed[9] to unfavorable interactions between alkyl groups (R_4 and R_1 or R_2) in the *trans* form of the ketene.

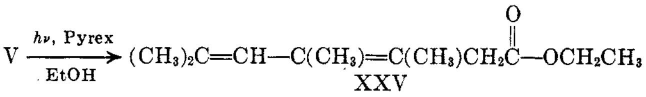


XXIV XXII XXIII

A novel photochemical path B has recently been discovered for completely substituted 2,4-cyclohexadienones (R_1–R_6 = Me or Et).[1] The product XXIV is formed by a bond crossing rather than an alkyl migration mechanism, as established by labeling experiments. In order to further define the structural requirements for this reaction, we photolyzed V.

Irradiation of V in anhydrous or wet ether, at 15° or at reflux, through Pyrex or Vycor for 10–15 hr with a 200-w Hanovia S mercury lamp led to no diminution in the concentration of V present, as determined by the ultraviolet spectra of samples withdrawn at various intervals. Under similar conditions, II is rapidly converted to XXIV (R_1–R_6 = CH_3).

However, irradiation of V in 95% ethanol through Pyrex at 15° led to rapid photolysis, complete in 2 hr. The major product (92%) was ethyl 3,4,6-trimethylhepta-3,5-dienoate (XXV). The infrared spectrum



$$V \xrightarrow[\text{EtOH}]{h\nu,\ \text{Pyrex}} (CH_3)_2C{=}CH{-}C(CH_3){=}C(CH_3)CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_2CH_3$$

XXV

showed ester carbonyl at 1725 cm^{-1}. The nmr spectrum is consistent only with the isomer in which the double bonds are placed as shown. In particular, a two-proton singlet at τ 7.07 must be due to α-methylene group, and there is only one vinyl hydrogen (τ 4.38). Four allylic methyls appear between τ 8.23 and 8.47, and the characteristic ethyl quartet and triplet are at τ 5.95 and 8.77, respectively.[11]

One may draw several conclusions from the present photolysis results. Rather subtle structural changes seem to determine whether path A or B is followed in 2,4-cyclohexadienone photolyses. For path B, either R_3 or R_6 or both cannot be hydrogen; which of these alternatives is correct is being investigated. Finally, the rather dramatic contrast in photochemical behavior of V in moist ether and ethanol suggests that polar or protonic solvents are particularly beneficial in Barton-type ring openings.

Experimental Section

Ultraviolet spectra were obtained on either a Cary Model 14 or a Beckman Model DB spectrophotometer; a Unicam Model SP-200 infrared spectrometer and a Varian A-60 spectrometer were used for infrared and nmr spectra. All infrared spectra were calibrated (polystyrene). Nmr chemical shifts are τ values, measured from tetramethylsilane as an internal reference. Elemental analyses are by Spang Microanalytical Laboratories, Ann Arbor, Mich. Melting points are uncorrected.

Oxidation of Durene to 3,4,6,6-Tetramethylcyclohexa-2,4-dienone (V).—A solution of peroxytrifluoroacetic acid,[12] prepared from 2.72 ml of 90% hydrogen peroxide (0.10 mole) and 23.2 g (0.11 mole) of trifluoroacetic anhydride in 25 ml of freshly distilled methylene chloride, was added with stirring over 40 min to a solution of 10.9 g (0.081 mole) of durene in 160 ml of methylene chloride, the mixture being kept below 8°. Boron fluoride (0.1 mole) was bubbled through the mixture concurrent with the addition of peracid. After further stirring for 1 hr at 5°, 50 ml of water was added, the aqueous phase was salted, and the organic layer was separated. The organic layer was washed with water (four 50-ml portions), saturated sodium bicarbonate (three 50-ml portions), Claisen's alkali[13] (four 50-ml portions), and water (two 50-ml portions), then dried over anhydrous

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[9] D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

[10] For reviews, see (a) G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965); (b) P. deMayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961); (c) O. L. Chapman, *Advan. Photochem.*, **1**, 344 (1963).

[11] From a study of the ultraviolet spectra of a number of heavily substituted 1,3-dienes which do not obey Woodward's rules, we are reluctant at the moment to assign stereochemistry to the double bonds. This question will be discussed more fully in a separate paper (with P. M. Collins).

[12] W. D. Emmons, *J. Am. Chem. Soc.*, **76**, 3468 (1954).

[13] Potassium hydroxide (100 g) in 100 ml of water, diluted to 400 ml with methanol.

magnesium sulfate. The residue after solvent removal on a rotary evaporator weighed 10.8 g. Vapor phase chromatography (5 ft × 0.25 in. SE-30 column, 170°, flow rate 67 ml/min of helium, Aerograph 90-P3) showed three components in order of increasing retention time: durene, **3,4,6,6-tetramethylcyclohexa-2,4-dienone** (V, 78.8% yield based on converted durene), and duroquinone (6%). Durene conversion was 67.4%. Duroquinone was identified by its melting point and infrared spectrum. The neutral products were separated by column chromatography on neutral alumina (Alcoa F-20, activated overnight at 205°) giving (eluent, ml, g of pure material): durene (pentane, 3000, 3.6), **dienone V** (ether, 800, 6.0), and duroquinone (1:1 ether–methanol, 500, 0.12).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.11; H, 9.40.

V showed a $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 316 mμ (log ϵ 3.36). Its infrared spectrum showed principal bands at 2975 (ν_{CH}), 1656 ($\nu_{\mathrm{C=O}}$), 1640 ($\nu_{\mathrm{C=C}}$), 1393 and 1380 (ν_{CH} deformation), and 860 cm^{-1} (vs, olefinic out-of-plane deformation). A weak band at 1568 cm^{-1} indicates a trisubstituted, conjugated alkene. The nmr spectrum of V (CCl_4 solution) showed a singlet at τ 8.93 (6 H, *gem*-dimethyl), two doublets at 8.08 and 7.96 (each 3 H split by low-field protons, J = 1.8 cps, allylic methyls), and two poorly resolved multiplets at 4.26 and 4.10 (each 1 H, vinyl protons). In an nmr tube, a sample (0.3 g) of V in 0.5 ml of CH_3OD was treated with a solution of 0.35 g of $NaOCH_3$ in 0.5 ml of CH_3OD. The peak at τ 7.96 disappeared completely; thus this peak is due to the allylic methyl on C-3.[1]

Dienone V (0.15 g), on treatment wih excess 2,4-dinitrophenylhydrazine in ethanol–phosphoric acid, gave 0.280 g (85%) of a dark red, crystalline 2,4-dinitrophenylhydrazone, mp 215.5–217°, $\lambda_{\max}^{\mathrm{EtOH}}$ 408 mμ (100 g ϵ 4.389).

The alkaline extracts from the oxidation work-up were combined and acidified with concentrated hydrochloric acid, and the organic products were extracted with ether. The residue, after washing with water and removal of solvent, consisted of 1.9 g of a viscous, brown oil. Analysis by vpc showed this material to consist of 0.96 g of 2,3,5,6-tetramethylphenol (XIII, 8%), 0.34 g of tetramethylhydroquinone (XIV, 2.6%), 0.035 g of 2,3,4,5-tetramethylphenol (0.3%), and 0.56 g of nonvolatile product. These products were identified by comparison of retention times and infrared spectra with those of authentic samples.

The durene oxidation was also carried out using boron fluoride–etherate in place of gaseous boron fluoride. From 8 g (0.06 mole) of durene and 0.07 mole of peroxytrifluoroacetic acid, with a work-up procedure as previously described, durene conversion was 82.5%. Based on this figure, the yields of products were V, 69.2%; XII, 3.9%; XIII, 14.5%; and XIV, 4.4%.

Oxidation of Durene with 90% Hydrogen Peroxide.—Durene (8.6 g, 0.064 mole) was suspended in a mixture of 100 ml of glacial acetic acid, 67 ml of concentrated sulfuric acid, and 17 ml of methylene chloride. A solution of 90% hydrogen peroxide (2.03 ml, 0.075 mole) in 23 ml of the same mixed acids was added with vigorous stirring over 15 min at room temperature. After 1.25 hr at 25°, the mixture was filtered through a medium glass fritted funnel to remove 2.95 g of undissolved durene. The filtrate was poured over 600 g of crushed ice and extracted with methylene chloride (three 100-ml portions). The organic layer was washed successively with water (two 100-ml portions), saturated sodium bicarbonate (two 100-ml portions), and water (100 ml), then dried. The residue after removing the solvent consisted of 6.35 g of light red-brown, mushy crystals. Quantitative vpc showed the durene conversion to be 50%; based on this conversion, the yields of products were: V, 52%; XII, 35%; XIII, 4.5%; XIV, 2.9%; and a minor, unidentified product, 5%. Products were identified by retention time and/or infrared spectra.

Maleic Anhydride Adduct of the Dienone.—A solution of 0.30 g of dienone V and 0.20 g of maleic anhydride in 5 ml of benzene was refluxed for 6 hr. Addition of petroleum ether (bp 30–60°) and cooling led to the isolation of 0.28 g of a white, crystalline adduct XI, mp 113–114°, from an ether–pentane mixture.

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.52; H, 6.43.

Major bands in the infrared spectrum included three at 1710 (unconjugated $\nu_{\mathrm{C=O}}$), 1768 and 1853 cm^{-1} (anhydride $\nu_{\mathrm{C=O}}$). The nmr spectrum (in $CDCl_3$) contained a singlet at τ 8.90 (6 H, *gem*-dimethyl), two broad bands at 8.15 and 8.10 (6 H, allylic methyls), a doublet at 7.05 (1 H, J = 3.2 cps), and a complex multiplet between 6.63 and 6.40 (3 H).

Reaction of Dienone V with Methylmagnesium Iodide.—To a solution of 1.0 g (6.7 mmoles) of 3,4,6,6-tetramethylcyclohexa-2,4-dienone (V) in 10 ml of anhydrous ether was added, with efficient stirring, 6.0 ml of a 1.4 *M* ethereal solution of methylmagnesium iodide (8.4 mmoles). After 15 min of reflux, the mixture was hydrolyzed by slow addition of saturated ammonium chloride. Ether (50 ml) was added, the aqueous layer was salted, and the separated organic phase was washed with water and dried. Removal of the solvent left 0.92 g of a pale yellow oil. Vpc (10 ft × 0.25 in. SE-30 column, 180°, 80 ml/min helium flow rate) led to the isolation of two products, listed in order of retention time. (1) The infrared spectrum of **1,3,3,4-tetramethyl-6-methylenecyclohexa-1,4-diene** (**XVIII**) (89%) showed major peaks at 885 (vs, terminal methylene), 1360, 1380, and 1445 (ν_{CH}, *gem*-dimethyl), 1584 and 1663 cm^{-1} (internal $\nu_{\mathrm{C=C}}$). It had a $\lambda_{\max}^{\mathrm{EtOH}}$ 248 mμ (log ϵ 3.63). The nmr spectrum had a singlet at τ 8.92 (6 H, *gem*-dimethyl), a multiplet from 8.26 to 8.20 (6 H, allylic methyls), two singlets at 5.43 and 5.32 (each 1 H, terminal methylenes), and two broad multiplets at 4.64 and 4.21 (each 1 H, vinyl protons at C-5 and C-2, respectively). (2) Pentamethylbenzene (11%) had mp 51.5–53°, retention time and infrared and nmr spectra identical with those of authentic material.

Reduction of Dienone V with Lithium Aluminum Hydride.—A solution of 0.40 g (2.7 mmoles) of V in 10 ml of anhydrous ether was added slowly to a stirred suspension of 56 mg (1.5 mmoles) of lithium aluminum hydride in 10 ml of the same solvent. After 30 min of stirring at room temperature, 50 ml of wet ether was slowly added. Filtration removed the white precipitate, which was subsequently triturated with ether (three 20-ml portions). Combined organic extracts were dried and evaporated, giving 0.370 g (91.3%) of **3,4,6,6-tetramethylcyclohexa-2,4-dienol** (**XX**) as a yellow, mobile liquid. The infrared spectrum showed major peaks at 830 (trisubstituted olefinic CH out-of-plane deformation), 1360, 1380, and 1450 (*gem*-dimethyl), and 3370 cm^{-1} (bonded ν_{OH}). The nmr spectrum (CCl_4) had a singlet at τ 9.07 (6 H, *gem*-dimethyl), two doublets centered at 8.27 and 8.22 (6 H, J = 1.6 cps, allylic methyls at C-3 and C-4 split by vinyl protons at C-2 and C-5), a broad peak at 6.23 (1 H, > C-HO), and two rather broad peaks at 4.80 and 4.52 (each 1 H, vinyl protons).

Passage of XX though a gas chromatograph at 160° gave three products, listed in order of retention time. (1) **1,3,3-trimethyl-6-methylenecyclohexa-1,4-diene** (**XXI**) (79%) had an infrared spectrum with major bands at 878 (vs, terminal methylene $\delta_{\mathrm{CH_2}}$) 1357, 1373, and 1445 (*gem*-dimethyl), 1582 and 1655 cm^{-1} ($\nu_{\mathrm{C=C}}$, conjugated). The ultraviolet spectrum had $\lambda_{\max}^{\mathrm{EtOH}}$ at 247 mμ (log ϵ 3.84) and 221 mμ (log ϵ 3.16). The nmr spectrum of XXI had a singlet at τ 8.93 (6 H, *gem*-dimethyl), a doublet at 8.18 (3 H, J = 1.3 cps, allylic methyl split by adjacent vinyl proton), two broad bands at 5.28 and 5.13 (each 1 H, terminal methylene), a broad singlet at 4.53 (1 H, vinyl proton adjacent to methyl), and two doublets centered at 4.45 and 3.95 (each 1 H, J = 9.4 cps, two adjacent vinyl protons). (2) Durene (14.1%) had mp 77–78°. (3) Prehnitene was obtained in 7.2% yield. The retention times and infrared and nmr spectra of the last two products were identical with those of authentic material.

A solution of 50 mg of XX in 0.5 ml of ether was shaken with 3 drops of concentrated hydrochloric acid for a few minutes in an nmr tube. Integration of the nmr spectrum showed the only products to be XXI (44%), durene (29%), and prehnitene (27%). Similar rearrangement was noted when a solution of XX in CCl_4 was stored for several days.

Photolysis of V.—A solution of 1.96 g (13 mmoles) of V in 400 ml of 95% ethanol was irradiated through Pyrex at 15° using a 200-w Hanovia Type S mercury lamp. The photolysis, followed by disappearance of the ultraviolet band at 315 mμ, was complete (over 95%) in 2 hr. The major product (92%) was purified by vpc (10 ft × 0.25 in. SE-30 column, 173°, 75 ml/min of helium), and shown to be **ethyl 3,4,6-trimethylhepta-3,5-dienoate** (**XXV**). Its infrared spectrum had major bands at 1040, 1180 (aliphatic ester), 1725 (vs, $\nu_{\mathrm{C=O}}$), 1383, 1450 ($\delta_{\mathrm{CH_3}}$ deformation), 2930 and 2980 cm^{-1} (ν_{CH}). The nmr spectrum had a triplet at τ 8.77 (3 H, J = 7.2 cps, methyl of ethyl group), three peaks in the region 8.23–8.47 (12 H, allylic methyls), a singlet at 7.07 (2 H, methylene α to the carbethoxy group), a quartet centered at 5.95 (2 H, J = 7.2 cps, methylene of ethyl group), and a singlet at 4.38 (1 H, vinyl proton).