for 3 protons (methyl group).[27] *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.17; H, 9.86.

Preparation and Decomposition of 1-Diazo-4-(3,4-dihydro-1-naphthyl)-butan-2-one (VII).—β-(3,4-Dihydro-1-naphthyl)propionic acid, mp 105–108° (lit.[28] 105–107°), was converted to the acid chloride *via* the action of oxalyl chloride on the sodium salt, and the acid chloride was taken to the diazo ketone with ethereal diazomethane. An 18.0-g sample of the diazo ketone was dissolved in 1800 ml of cyclohexane, treated with copper powder, and refluxed for 18 hr. The solvent and catalyst were removed to

(27) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 1965 (1966), have obtained VI in yields up to 47% through the use of a copper-bronze catalyst and by operating on a considerably smaller scale. We are indebted to Professor Zimmerman for communicating these results to us prior to publication.

(28) W. S. Johnson, H. C. E. Johnson, and J. W. Peterson, *J. Am. Chem. Soc.*, **67**, 136 (1945).

leave a light brown oil containing some crystalline material. Filtration to remove the oily portion and one recrystallization of the solid residue yielded 3.5 g (22%) of colorless crystals, mp 94–96°. Additional crystallizations from petroleum ether (bp 63–69°) gave 5,5-benzotricyclo[5.3.0.0^{5,10}]decan-1-one (VIII) as colorless needles: mp 99–101°; ν_{max}^{CCl4} 1740 cm^{-1} (cyclopentanone carbonyl); λ_{max}^{EtOH} (ϵ) 235 mμ (8700). *Anal.* Calcd for $C_{14}H_{14}O$: C, 85.00; H, 7.08. Found: C, 84.84; H, 7.05.

A 0.75-g sample of VIII was treated with phenylmagnesium bromide, and the resulting alcohol was dissolved in xylene and treated with iodine to effect dehydration. The product from this treatment was mixed with 0.21 g of sulfur and heated for 2 hr at 380–400° to effect dehydrogenation. From the reaction mixture there was obtained 0.15 g of 2-phenylphenanthrene, mp 192–194° (lit.[29] mp 195–196°), which formed a 2,4,6-trinitrofluorenone derivative, mp 164–166° (lit.[29] mp 168.8–169.4°).

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Structural Features Facilitating the Photodecarbonylation of Cyclic Ketones[1,2]

J. EDWARD STARR AND RICHARD H. EASTMAN

Department of Chemistry of Stanford University, Stanford, California

A number of cyclic ketones have been synthesized and found to undergo facile photodecarbonylation in solution, a process which has been reported for only a relatively small number of ketones. It has been found that incorporation of certain structural features into a cyclic ketone, including β,γ-unsaturation, a cyclopropylcarbinyl system, and α-alkyl substitution, enables such a molecule to decarbonylate readily. An explanation for the influence of these structural features on photodecarbonylation has been advanced.

Of the various types of photochemical reactions exhibited by nonconjugated ketones in solution,[3,4] photodecarbonylation, a process which is well known in the gas phase,[5,6] has only recently been observed as an important pathway in solution. Among those ketones which do decarbonylate readily in the liquid phase are included *l*-thujone[7] (I), 3,5-cycloheptadienone[8] (III), ketone[9] IV, derivatives of 2-indanone[10] (V), derivatives of 1,3-cyclobutanedione[11] (VI), and bicyclo[5.2.1]decan-10-one[12] (VII) (Chart I).

The structural features facilitating decarbonylation suggested by these examples include a double cyclopropylcarbinyl system, β,γ-unsaturation, and α-alkyl substitution. In order to generalize the influence of the cyclopropane ring, as exhibited by *l*-thujone (I), and to determine whether the reaction can be extended to related systems, ketones XIV and XVI (Scheme I) and ketone XXIV (Scheme II) were prepared. In order to study the influence of α-alkyl substitution and a doubly

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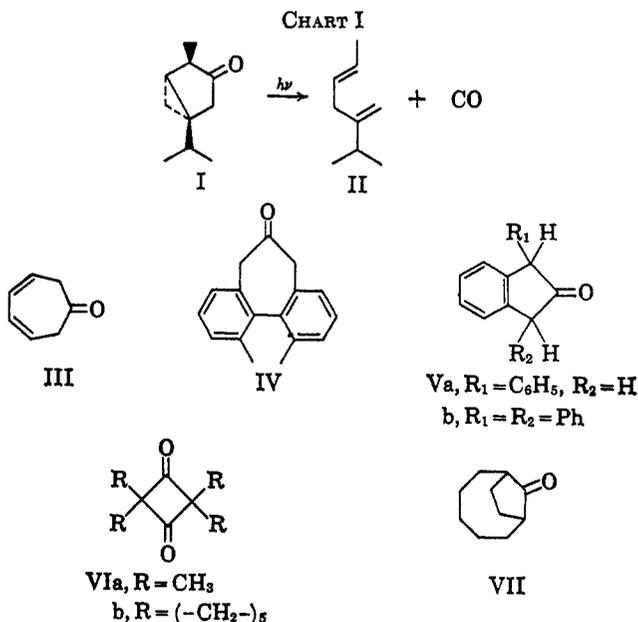
β,γ-double bond on liquid phase photodecarbonylation, ketones XXV, XXVI, and XXIX (Scheme III) and the readily available 2,2,6,6-tetramethylcyclohexanone (XXXVIII) were also prepared and photolyzed.

Results

I. Synthesis.—In order to prepare ketones XIV and XVI (Scheme I) containing, respectively, a cyclopropane and oxacyclopropane ring, it was considered that the unsaturated alcohol XII would be a convenient intermediate. The method of Horan and Schiessler[13]

(1) Based on the Ph.D. Thesis of J. E. Starr, Stanford University, 1965.

(2) The support of the Air Force Office of Scientific Research (AFOSR-62-116 and AF49 638-1272) is gratefully acknowledged.

(3) P. DeMayo, *Advances Org. Chem.*, **2**, 367 (1960).

(4) P. DeMayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961).

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(6) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

(7) R. H. Eastman, J. E. Starr, R. St. Martin, and M. K. Sakata, *J. Org. Chem.*, **28**, 2162 (1963).

(8) (a) O. L. Chapman and G. W. Borden, *ibid.*, **26**, 4185 (1961); (b) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

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(10) G. Quinkert, K. Opitz, W. W. Wiersdorff, and J. Weinlich, *Tetrahedron Letters*, 1863 (1963).

(11) (a) N. J. Turro, G. W. Byers, and P. A. Leermakers, *J. Am. Chem. Soc.*, **86**, 955 (1964); (b) P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, *ibid.*, **86**, 4213 (1964); (c) R. C. Cookson, J. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964).
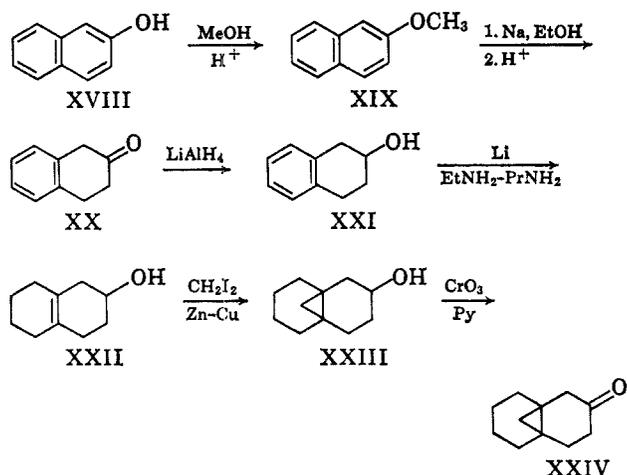
(12) C. D. Gutsche and C. W. Armbruster, *Tetrahedron Letters*, 1297 (1962).

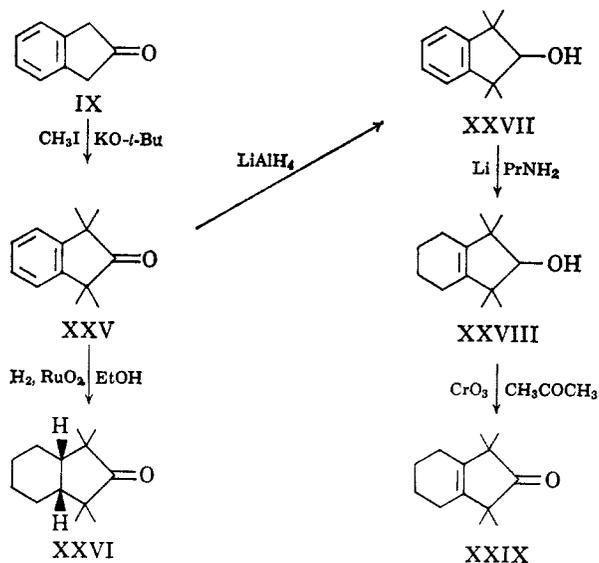(13) J. E. Horan and R. W. Schiessler, *Org. Syn.*, **41**, 53 (1961).

SCHEME I
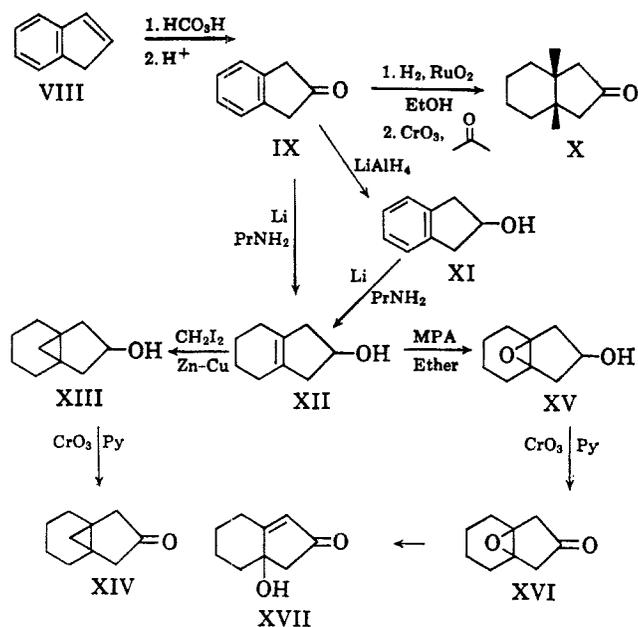
SCHEME II

SCHEME III

because spectra of the related ketones thujone (I) and bicyclo[3.2.1]hexan-3-one[16] do not contain such a band. Although the most likely explanation is that this band is due to the presence of a small amount of an undetected impurity in ketone XIV, the alternative possibility that the band in question was due to interaction of the cyclopropane ring electrons with the carbonyl group cannot be disposed of on the basis of the evidence at hand.

Epoxidation of the unsaturated alcohol XII with monoperphthalic acid in ether gave a high yield of 10-oxatricyclo[4.3.1.0^{1,6}]decan-8-ol (XV). The presence of two large spots with similar retention factors on a thin layer chromatogram suggested that XV was a mixture of cis- and trans-epoxy alcohols. Without purification, XV was oxidized with chromium trioxide–pyridine complex[17] to the corresponding ketone (XVI) in 20–37% yield. The ultraviolet spectrum in ethanol showed that a saturated ketone group was present [λ_{max} 283 mμ (ϵ 18)] and also exhibited a short wavelength band [202.5 mμ (ϵ 197)] similar to the band in the spectrum of XIV (see above). A third band at ca. 230 mμ (ϵ 50) was due to the presence of a small amount of an isomerization product (XVII) which was found to be produced from XVI by distillation at aspirator pressure or chromatography on silica gel G. It was also later found that XVI slowly isomerizes to XVII on standing at room temperature.

The structure of the unsaturated hydroxy ketone (XVII) rests on the infrared [ν_{max}^{KBr} 1670, 1616, 862, 829, 811 (–C=CHC=O), and 727 cm^{-1} ((–CH$_2$–)$_4$); $\nu_{max}^{CHCl_3}$ 4415 cm^{-1} (OH)] and ultraviolet spectra [λ_{max}^{EtOH} 225 and 308 mμ (ϵ 12,900 and 95, respectively)]; the ultraviolet spectrum was similar to that of bicyclo[4.3.0]non-6-en-8-one[18] [228 mμ (ϵ 16,500)]. The pmr spectrum of XVII demonstrated the presence of a single vinyl proton (δ 5.78) and a hydroxyl proton (δ 3.20); the latter absorption disappeared under deuterium-exchange conditions. The two protons adjacent to the carbonyl group appeared as a singlet at δ 2.44. The absence of

was employed to prepare 2-indanone (IX) from indene (VIII). Reduction of 2-indanone with lithium and n-propylamine[14] gave only a 9% yield of the unsaturated alcohol XII accompanied by a large amount of tarry by-product, but when ketone IX was first reduced to 2-indanol (XI) using lithium aluminum hydride, the latter could be reduced with lithium and n-propylamine to give an 85% yield of 4,5,6,7-tetrahydro-2-indanol (XII).

Tricyclo[4.3.1.0^{1,6}]decan-8-ol (XIII) was prepared from XII in 42% yield using diiodomethane and zinc–copper couple[15] in ether. Analytical and spectral data (see Experimental Section) are in accord with the assigned structure. Sarett oxidation of XIII gave tricyclo[4.3.1.0^{1,6}]decan-8-one (XIV) in 72% yield. The ultraviolet spectrum, λ_{max}^{EtOH} 285 mμ (ϵ 19.6), indicated the presence of a saturated ketone group and exhibited a second weak absorption band at 211.5 mμ (ϵ 172). The appearance of this latter band was not expected

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(15) H. E. Simmons and R. D. Smith, J. Am. Chem. Soc., 80, 5323 (1958); 81, 4256 (1959).

(16) S. Winstein and J. Sonnenberg, ibid., 83, 3235 (1961).

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absorption which could be assigned to a proton on carbon bearing oxygen indicated that the hydroxyl group is tertiary. The total integral was in accord with structure XVII.

In order to demonstrate that the bicyclo[4.3.0]nonane ring system, which is present in a number of the ketones described in this paper, does not in itself facilitate the photodecarbonylation of a ketone, cis-2-hydrindanone (X) was prepared by catalytic hydrogenation of 2-indanone (IX) over ruthenium dioxide in ethanol, followed by oxidation of the product with chromium trioxide in acetone.

Tricyclo[4.4.1.0^{1,6}]undecan-3-one (XXIV) was prepared by the route indicated in Scheme II. β-Naphthol was methylated by the procedure of Stork.[19] β-Tetralone (XX) was prepared from XIX by the procedure of Soffer, et al.,[20] and was in turn reduced to β-tetralol (XXI) using lithium aluminum hydride. Reduction of XXI using lithium and ethylamine–n-propylamine[14b] gave 1,2,3,4,5,6,8-octahydro-2-naphthol (XXII) in 78% yield.

Treatment of alcohol XXII with diiodomethane and zinc–copper couple in ether gave tricyclo[4.4.1.0^{1,6}]-undecan-3-ol (XXIII) in 61% yield. Sarett oxidation of XXIII gave the desired tricyclic ketone (XXIV). Spectral data (see Experimental Section) are in accord with the assigned structure.

The three tetramethyl ketones XXV, XXVI, and XXIX were synthesized by the route indicated in Scheme III. Methylation of 2-indanone (IX) with methyl iodide and potassium t-butoxide gave 1,1,3,3-tetramethyl-2-indanone (XXV) in 71% yield.

Catalytic hydrogenation of XXV over ruthenium dioxide in ethanol gave a 51% yield of 1,1,3,3-tetramethyl-cis-2-hydrindanone (XXVI). The cis ring juncture assignment was made on the basis of analogy with the product obtained by hydrogenation of 2-indanone (see above) and on the basis of the relatively narrow half-width (7.5 cps) of the pmr band due to the methylene protons (see Experimental Section for spectral data). If the rings in XXVI were fused trans, the rigidity of the six-membered ring would lead to distinct axial and equatorial protons whose coupling should lead to an absorption band with a relatively greater half-width.[21]

Reduction of ketone XXV with lithium aluminum hydride in ether gave an essentially quantitative yield of the corresponding alcohol (XXVII). Reduction of XXVII with lithium and n-propylamine proceeded only with difficulty, but repeated reduction eventually led to a mixture of XXVII and XXVIII which was oxidized with chromium trioxide in acetone to a mixture of XXV and XXIX. The desired ketone 1,1,3,3-tetramethyl-4,5,6,7-tetrahydro-2-indanone (XXIX) was separated from the mixture by preparative vapor phase chromatography.

The synthesis of 2,2,6,6-tetramethylcyclohexanone (XXXVIII) was carried out by oxidation of 2-methylcyclohexanol[22] followed by repeated methylation of the product with sodium amide and methyl iodide by a procedure similar to that described by Fischer and Wunderlich.[23]

II. Photolysis.—The results of irradiation of cyclohexane solutions of the ketones whose syntheses have been described above are shown in Scheme IV. The photolyses were carried out in quartz apparatus in a nitrogen atmosphere using the unfiltered radiation provided by a high-pressure mercury arc. Yields of products were determined by gas chromatography, and in most cases the isolated yields were quite good. The products from each reaction were isolated by preparative gas chromatography, and structures were determined by physical methods (see below).
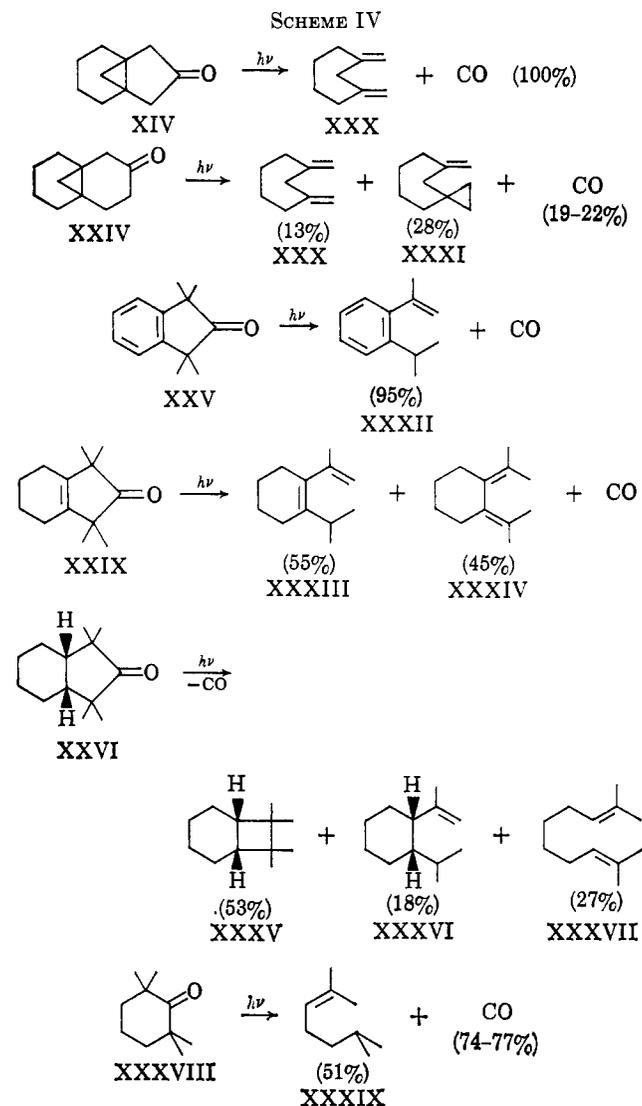
SCHEME IV

In contrast to the results shown in Scheme IV, irradiation of cis-2-hydrindanone (X) gave only a small yield (11–22%) of carbon monoxide, and the only volatile components which could be detected in the yellow photolysate by gas chromatography were unreacted ketone and solvent.

Irradiation of the epoxy ketone XVI in either cyclohexane or methanol gave small amounts (less than 0.2 mole/mole of ketone) of a mixture of carbon monoxide and carbon dioxide. The product consisted of a tarry fraction (ca. 50%) and a volatile fraction containing

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(20) M. D. Soffer, M. P. Bellis, H. E. Gellerson, and R. A. Stewart, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 903.
(21) W. B. Moniz and J. A. Dixon, J. Am. Chem. Soc., 83, 1671 (1961).
(22) E. W. Warnhoff, D. G. Martin, and W. S. Johnson, ref 20, p 164.
(23) F. G. Fischer and K. Wunderlich, Ber., 74, 1544 (1941).

mainly unreacted ketone along with small amounts of a number of products which were not identified.

Tricyclo[4.3.1.0^{1,6}]decan-8-one (XIV).—The structure 1,3-dimethylenecycloheptane (XXX) was assigned to the photoproduct from irradiation of ketone XIV on the following basis: the ultraviolet spectrum of XXX showed only strong end absorption (ϵ_{212} 5,200) thus ruling out the possibility of a conjugated diene; the infrared spectrum indicated the presence of two terminal methylene groups [3068, 2979, 1635 (doublet), and 888 (with slight shoulder) cm^{-1}]. The pmr spectrum showed two complex absorptions centered at δ 1.60 and 2.17 (regular methylene and allylic methylene protons, respectively), a sharp signal with fine splittings at δ 3.02 (doubly allylic methylene protons), and a singlet at δ 4.74 (vinyl protons) in accord with structure XXX. Areas under absorption bands in this spectrum and in all spectra reported in this section are in accord with assignments given.

Tricyclo[4.4.1.0^{1,6}]undecan-3-one (XXIV).—The first product isolated from photolysis of ketone XXIV was found to be identical (infrared and pmr spectroscopy) with diene XXX obtained from photolysis of ketone XIV. The second product was assigned the structure 5-methylenespiro[2,6]nonane (XXXI). The ultraviolet spectrum of XXXI showed only end absorption, and the infrared spectrum indicated the presence of a cyclopropane ring (3061 and/or 2987, and 1012 cm^{-1}) and a terminal methylene group (1639 and 882 cm^{-1}). The pmr spectrum consisted of a four-proton singlet at δ 0.30 (cyclopropane), a complex six-proton absorption centered at δ 1.53 (-CH$_2$-), a two-proton singlet at δ 2.16 (allylic methylene group adjacent to cyclopropane ring), a broad two-proton absorption at δ 2.35 (allylic methylene group), and two one-proton singlets (with fine structure) at δ 4.59 and 4.67 (vinyl protons) in accord with structure XXXI.

1,1,3,3-Tetramethyl-2-indanone (XXV).—The photoproduct from photolysis of ketone XXV was assigned the structure o-isopropyl-α-methylstyrene (XXXII). A molecular weight determination demonstrated that the product was monomeric. The infrared spectrum indicated the presence of an *ortho*-disubstituted benzene ring (1598, 1487, and 765 cm^{-1}), a terminal methylene group (1640 and 893 cm^{-1}), and a *gem*-dimethyl group (1381 and 1369 cm^{-1}). The ultraviolet spectrum in ethanol [λ_{max} 262 and 269 mμ (log ϵ 2.47 and 2.37, respectively)] was similar to that of α,2,4,6-tetramethylstyrene[24] [λ_{max} ca. 270 mμ (log ϵ ca. 2.4)] in which a normal styrene spectrum is also not observed because of steric hindrance to coplanarity of the two chromophores. The pmr spectrum consisted of a six-proton doublet at δ 1.20 (J = 6 cps, CH_3CHCH_3), a three-proton doublet at δ 2.02 (J = 1 cps, C=C-CH_3), a one-proton septet at δ 3.17 (J = 6 cps, CH$_3$CHCH$_3$), two one-proton multiplets at δ 4.80 and 5.14 (C=CH_2), and two two-proton multiplets at δ 7.05 and 7.21 (aromatic) in accord with structure XXXII.

Photolysis of ketone XXV in tetrahydrofuran-d_8 or in cyclohexene gave essentially the same results as were obtained in cyclohexane, and the product was shown to contain no deuterium by careful integration of its pmr spectrum. When ketone XXV was irradiated in isopropyl alcohol, gas evolution proceeded at a consider-

ably slower rate, and the gas (81%) contained a trace of methane in addition to carbon monoxide. The major product was again hydrocarbon XXXII (78%), and unreacted ketone (13%) was also present. Several minor products (which had been observed in the photolyses run in hydrocarbon solvents) were also present in addition to 1,1,3,3-tetramethyl-2-indanol (XXVII) and acetone (identified by comparison of gc retention times with those of authentic samples). These latter two products had not been observed in previous photolyses and were probably formed by photochemical reduction of ketone XXV by isopropyl alcohol, a process which has been widely observed in other systems.[25]

1,1,3,3-Tetramethyl-4,5,6,7-tetrahydro-2-indanone (XXIX).—The first photoproduct from irradiation of ketone XXIX was assigned the structure 1-isopropenyl-2-isopropylcyclohexene (XXXIII). The infrared spectrum indicated the presence of a *gem*-dimethyl group (1366 and 1355 cm^{-1}), a terminal methylene group (1625 and 886 cm^{-1}), and a second double bond (1650 cm^{-1}, weak) lacking vinyl hydrogen atoms (no out-of-plane bending bands). The ultraviolet spectrum in cyclohexane showed only a shoulder on the end absorption [ca. 225 mμ (ϵ 1960)]. Examination of a model of diene XXXIII indicates that steric interactions between the isopropyl and isopropenyl groups would prevent coplanarity of the two double bonds, which would be expected to give rise to an anomalous ultraviolet spectrum as is observed. The pmr spectrum consisted of a six-proton doublet at δ 0.92 (J = 7 cps, CH_3CH-CH_3), a complex four-proton absorption at δ 1.58 (CH_2), a three-proton doublet at δ 1.77 (J = 1 cps, C=C-CH_3), a complex four-proton absorption at δ 1.96 (C=C-CH_2)-), a one-proton septet at δ 2.83 (J = 7 cps, CH$_3$CHCH$_3$), and two one-proton multiplets at δ 4.60 and 4.81 (C=CH_2) in accord with structure XXXIII.

The second photoproduct was assigned the structure 1,2-diisopropylidinecyclohexane (XXXIV). The infrared spectrum showed only bands characteristic of a saturated hydrocarbon, and the ultraviolet spectrum in cyclohexane exhibited no maxima above 207 mμ, although strong end absorption was present (ϵ_{210} 12,800). Nazarov and Kuznetzov[26] have previously reported a synthesis of diene XXXIV, and they reported λ_{max} 259.5 mμ (log ϵ 2.877). However, because of the vigorous conditions of their preparation, it seems possible that their product may have been contaminated with an isomer for which such an absorption would be expected. Compounds similar to XXXIV are known to exhibit anomolous ultraviolet spectra.[27] The pmr spectrum of XXXIV consisted of two six-proton singlets at δ 1.52 and 1.68 (C=C-CH_3) superimposed on a broad six-proton absorption from ca. δ 1.25 to 2.00 (four regular and two allylic methylene protons). The remaining two allylic protons are not equivalent to the first two and appear as two broad one-proton singlets at δ 2.58 and 2.73. Examination of a model of diene XXXIV indicates that the conformation which possesses the fewest destabilizing steric interactions is a chair

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(27) (a) W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953); (b) A. T. Blomquist and D. T. Longone, *ibid.*, **79**, 3916 (1957); (c) W. J. Bailey, R. L. Hudson, and C.-W. Liao, *ibid.*, **80**, 4358 (1958); (d) W. J. Bailey and R. L. Hudson, *ibid.*, **78**, 2806 (1956).

form in which the double bonds are noncoplanar, two of the allylic methylene protons are approximately in the plane of the adjacent double bond, and two allylic methylene protons are approximately at right angles to the plane of the adjacent double bond. Final confirmation of the structure of this product was obtained by ozonolysis to give 1,2-cyclohexanedione and acetone.

1,1,3,3-Tetramethyl-*cis*-2-hydrindanone (XXVI).— The major photoproduct from photolysis of ketone XXVI was assigned the structure 7,7,8,8-tetramethyl *cis*-bicyclo[4.2.0]octane (XXXV). The infrared spectrum exhibited only bands characteristic of a saturated hydrocarbon, and a molecular weight determination demonstrated that the product was monomeric. The ultraviolet spectrum showed only weak end absorption (ϵ_{210} 150). The pmr spectrum consisted of a 12-proton singlet at δ 0.93 (CH_3), a complex eight-proton absorption centered at δ 1.42 (CH_2), and a broad two-proton absorption at δ 1.97 (bridgehead protons). The *cis* stereochemistry was assigned on the basis of the relatively narrow half-width of the pmr absorption band for the methylene protons (11 cps) and on the reasonable assumption that the photoprocess leading to XXXV involved cleavage only of the bonds adjacent to the carbonyl group in ketone XXVI.

Products XXXVI and XXXVII were found to have almost identical gas chromatographic retention times. Product XXXVII was obtained in pure form, but the physical measurements pertinent to structure XXXVI were made on a mixture of XXXVI and XXXVII containing *ca*. two-thirds of the former. The assignments of spectral bands to compound XXXVI were made by visually subtracting the bands due to XXXVII from the spectra of the mixture. Combustion analysis of a mixture of XXXVI and XXXVII gave satisfactory results for $C_{12}H_{22}$, indicating that the two products are isomeric. The ultraviolet spectrum of the same mixture showed only end absorption. The infrared spectrum of XXXVII indicated the presence of a trisubstituted double bond [3040, 1650 (br), and 822 cm^{-1}]. The pmr spectrum consisted of a complex four-proton absorption at δ 1.32 (CH_2), two six-proton singlets at δ 1.61 and 1.70 (C=C—CH_3), a complex four-proton absorption at *ca*. δ 2.0 (C=C—CH_2), and a two-proton triplet (with fine structure) at δ 5.13 (J = 7 cps, C=C—H) in agreement with the structure 2,9-dimethyl-2,8-decadiene for compound XXXVII.

The infrared spectrum of XXXVI indicated the presence of a terminal methylene group (3090, 3070, 1633, and 882 cm^{-1}). The pmr spectrum consisted of two three-proton doublets at δ 0.87 and 0.90 (J = 6.2 cps, CH_3CHCH_3), a three-proton doublet at δ 1.78 (J = 1 cps, C=C—CH_3), a broad one-proton band at δ 2.27 (C=C—CH), and a two-proton singlet (with fine structure) at δ 4.80 (C=CH_2) which split into two bands at 100 Mc. Careful integration demonstrated that the remaining ten protons were buried under the absorptions due to the other component (XXXVII) of the mixture between *ca*. δ 1.08 and 1.92. The visible features of this spectrum are well in accord with structure XXXVI, 1-isopropenyl-2-isopropylcyclohexane. The *cis* stereochemistry was assigned on the assumption that the bonds to the bridgehead carbon atoms in ketone XXVI were not broken in the process leading to XXXVI.

When ketone XXVI was photolyzed in isopropyl alcohol, gas evolution proceeded at a much slower rate, and the gas (3.16 moles/mole of ketone) consisted of a mixture of carbon monoxide and methane. The major components of the photolysate were again hydrocarbons XXXV, XXXVI, and XXXVII and a new product which was found to be 2,3-dimethyl-2,3-butanediol (pinacol). The ratio XXXV:(XXXVI + XXXVII): pinacol was *ca*. 9.4:1.0:15.7. [The ratio XXXV: (XXXVI + XXXVII) obtained by photolysis of ketone XXVI in cyclohexane was *ca*. 6:5; no definite explanation is presently available for the solvent dependency of this ratio.]

2,2,6,6-Tetramethylcyclohexanone (XXXVIII).—Irradiation of ketone XXXVIII gave a mixture of at least seven photoproducts. The major component (51%) was isolated and assigned the structure 2,6-dimethyl-2-heptene (XXXIX). The ultraviolet spectrum showed only end absorption, and the infrared spectrum indicated the presence of a trisubstituted double bond [3035, 3010, 1650 (br), and 810 cm^{-1}] and a *gem*-dimethyl group. The pmr spectrum consisted of a six-proton doublet at δ 0.88 (J = 5 cps, CH_3CHCH_3), two broadened three-proton singlets at δ 1.60 and 1.69 (C=C—CH_3), and an apparent triplet (with fine structure) at δ 5.12 (one proton, C=CH-). The methine proton and the two ordinary methylene protons appeared in a complex pattern from *ca*. δ 1.0 to 1.6, and the two allylic methylene protons appeared in a complex pattern from *ca*. δ 1.75 to 2.2.

A comparison of the rates of photodecarbonylation of ketones XXV, XXIX, and XXVI is shown in Table I. The photolyses from which these data are taken were all run under the same conditions using the same sample cell and light source.

TABLE I

PHOTOCHEMICALLY INDUCED ELIMINATION OF CARBON
MONOXIDE FROM TETRAMETHYL KETONES IN CYCLOHEXANE[a,b]

Compd (mmoles × 10³)	% of theoretical gas evolved in 5.0 hr
XXC (1.58)	86
XXIX (1.41)	98
XXVI (1.65)	41[c]

[a] The volume of solvent was 5.0 ml in each case. [b] The initial concentrations and the path length (0.65 cm) were such as to provide an optical density of *ca*. 3.5 (295 mμ) at the outset of photolysis, ensuring complete absorption of radiation in the n → π^* region during the majority of reaction. [c] After 10.0 hr, 71% carbon monoxide was obtained, and, after 15.0 hr, the yield was 84%.

Discussion

The fact that thujone (I) and the tricyclic ketone XIV both undergo smooth photodecarbonylation to analogous products strongly implies participation of the cyclopropane rings in facilitating the elimination of carbon monoxide. It seems reasonable to suppose that the driving force for the reaction lines in strain relief obtained by cleavage of the cyclopropane ring. The reasons for the failure of the related epoxy ketone XVI to undergo a similar reaction are not immediately apparent. Clearly the epoxy ketone is not stable to ultraviolet radiation, but the predominant mode of decomposition apparently leads to polymeric products, most of which are not formed *via* loss of carbon monoxide. The expected photoproduct from ketone XVI would be a

divinyl ether; its polymerization under these conditions would not be too surprising. However, this cannot be the complete explanation since considerably more polymerization occurred than decarbonylation.

The results of irradiation of XXIV, in which the carbonyl group carries but a single cyclopropylcarbinyl system, are only partially similar to the results obtained with ketones I and XIV. The formation of diene XXX represents a formal loss of ketene (C_2H_2O) from ketone XXIV. Although ketene was not detected in the photolysate (no exhaustive attempt was made to detect it), the formation of diene XXX strongly implies its formation. Several reports of photochemical elimination of ketene have appeared recently.[28]

The formation of photoproducts XXX and XXXI can be rationalized by the intermediation of a biradical such as XL, which could be produced from XXIV either by concerted or stepwise cleavage of both the bond α-to the carbonyl group and the cyclopropane ring. Cleavage of bond a in XL would lead to production of ketene and the diene XXX, whereas cleavage of bond b would result in the formation of carbon monoxide and the spirane XXXI (Chart II). Another possible transformation which one might predict for a species such as XL is cyclization to the spiro ketone XLI. This compound was not isolated from the photolysis of XXIV but it is interesting to note that the infrared spectrum of the crude photolysate exhibited an absorption band at 1789 cm^{-1}, characteristic of cyclobutanones, suggesting the possibility that XLI may have been among the several minor photoproducts which were not isolated from the reaction.

CHART II

XXIV   XLI

CH_2CO + XXX ← a — XL — b → CO + XXXI
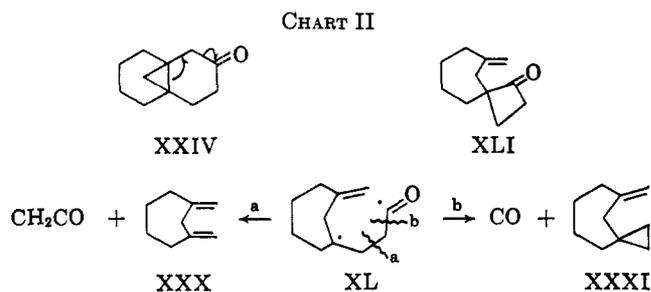
Turning to the photolyses of the tetramethyl ketones in Scheme IV, one may first consider the nature of the hydrogen transfer process leading to products XXXII, XXXIII, XXXVI, and XXXIX. One can visualize a process involving abstraction of hydrogen from the solvent by an intermediate such as XLII, followed by loss of hydrogen to a solvent-derived radical. That such a process does not occur is demonstrated by the fact that no deuterium was incorporated into the product when ketone XXV was irradiated in tetrahydrofuran-d_8. A similar intermolecular process between two biradicals such as XLII or between XLII and XXV could also be visualized, but this would be expected to lead to appreciable amounts of XLIII and XLIV. No evidence for the formation of these products has been obtained. Therefore, it is highly probable that the formation of XXXII involves a direct intramolecular hydrogen transfer in a cyclic six-membered

CHART III

XXV   XLII   XXXII

XLIII   XLIV   XLV
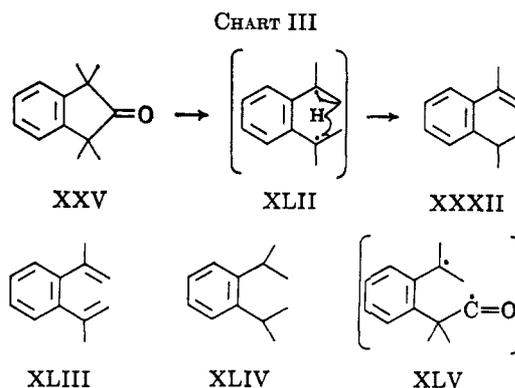
transition state such as that shown in Chart III. No evidence is presently available which would permit a distinction between direct formation of XLII from XXV by simultaneous rupture of both bonds α to the carbonyl group, or prior cleavage of only one such bond to give an intermediate such as XLV. The intermediation of biradicals similar to XLII would explain the formation of all the products isolated from irradiation of the tetramethyl ketones in Scheme IV. However, in the case of ketone XXXVIII there exists no possibility for a hydrogen transfer reaction involving a six-membered transition state, and the formation of olefin XXXIX probably is the result of an intramolecular hydrogen transfer involving a five-membered transition state.

The absence of the conjugated diene XLVI from photolysis of XXV may be due to the loss of aromatic resonance energy required for its formation; alterna-

XLVI   XLVII
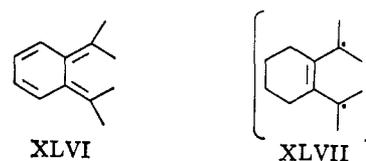
tively, it may itself be photochemically unstable. The absence of a product analogous to XXXV from irradiation of ketones XXV and XXIX may be due to the fact that the radicals in an intermediate of type XLVII would conjugate and thus are probably in the wrong geometry for ring closure.

The observation (Table I) that ketones XXV and XXIX, which contain homoallylic unsaturation, photodecarbonylate at a considerably faster rate than the saturated ketone (XXVI) indicates that the presence of homoallylic unsaturation facilitates the elimination of carbon monoxide from a cyclic ketone. This conclusion is supported by the reported photodecarbonylations of ketones III and IV.

The formation of pinacol during the photolysis of ketone XXVI in isopropyl alcohol probably arises from the dimerization of 2-hydroxy-2-propyl radicals formed by abstraction of hydrogen atoms from isopropyl alcohol by electronically excited ketone molecules. A common example of such a hydrogen transfer process is the photoreduction of ketones by alcohols.[29] Hammond[29c] has cited evidence for the formation of 2-hydroxy-2-propyl radicals produced by the irradiation of

(28) (a) W. H. Urry, D. J. Trecker, and D. A. Winey, Tetrahedron Letters, 609 (1962); (b) G. O. Schenck and R. Steinmetz, Ber., 96, 520 (1963); (c) D. I. Schuster, M. Axelrod, and J. Auerbach, Tetrahedron Letters, 1911 (1963); (d) J. C. Anderson and C. B. Reese, ibid., 1 (1962).

(29) (a) A. Schonberg and A. Mustafa, Chem. Rev., 40, 181 (1947); (b) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, C. Rectenwald, and R. B. Martin, J. Am. Chem. Soc., 81, 1068 (1959); (c) W. M. Moore, G. S. Hammond, and R. P. Foss, ibid., 83, 2789 (1961).

benzophenone in isopropyl alcohol. It has been noted (see above) that a large amount of methane also accompanied the formation of pinacol during the irradiation of XXVI in isopropyl alcohol. Since no other product could be detected in an amount sufficient to account for all the 2-hydroxy-2-propyl radicals formed, it is suggested that radical XLVIII (formed by photoreaction of XXVI with isopropyl alcohol) may lose a methyl radical to form enol XLIX which in turn tautomerizes to ketone L (Scheme V). Ketone L could be further

SCHEME V
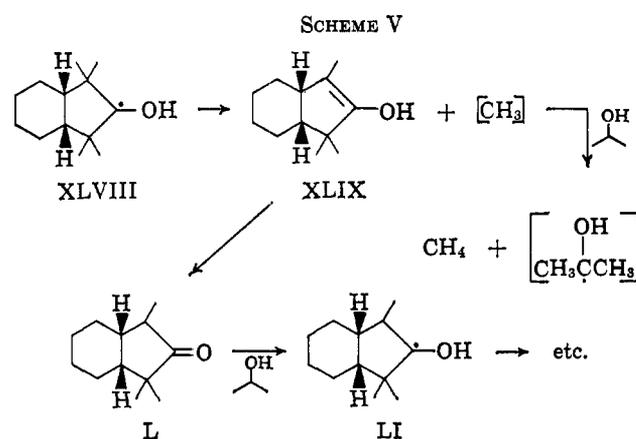
demethylated by the same process (*via* radical LI). The methyl radical could abstract a hydrogen atom from isopropyl alcohol to form methane and another 2-hydroxy-2-propyl radical. This mechanism therefore predicts that the source of at least part of the observed methane is the methyl groups of ketone XXVI, a prediction would could be tested by the use of ketone XXVI in which the methyl groups had been introduced using deuterated methyl iodide. This experiment has not been performed. Alternatively, the source of methane may have been acetone, from semipinacol radical disproportionation. It was not possible to determine whether acetone was among the photoproducts from irradiation of ketone XXVI in isopropyl alcohol. When ketone XXV was irradiated in isopropyl alcohol, acetone was found to be one of the photoproducts; however, in this case only a trace of methane was formed, and the presence or absence of pinacol was not established. It should be noted that the durations of photolyses of ketones XXV and XXVI in isopropyl alcohol were widely different, a fact which may affect the amounts of solvent-derived products formed.

The results described in this paper clearly demonstrate that the presence of a suitably located cyclopropane ring, β,γ-unsaturation and α-alkyl substitution definitely facilitate the photochemical elimination of carbon monoxide from a cyclic ketone. A reasonable explanation for the influence of α-alkyl substitution and unsaturation in facilitating photodecarbonylation is that these structural features are capable of stabilizing a biradical intermediate such as XLVII (see above), which would result from loss of carbon monoxide from a ketone. From the reported observation[12] that ketone VII does photodecarbonylate in solution, whereas the similarly alkyl-substituted ketone 2,6-dimethylcyclohexanone does not, it is not clear as to what factors determine how much α-alkyl substitution is necessary to promote liquid phase photodecarbonylation. Further experimentation will be necessary to clarify this point.

Experimental Section

General.—Melting points were taken using a Thomas capillary melting point apparatus or a Monoscop IV hot stage. Proton magnetic resonance spectra were recorded on a Varian HR-60 instrument in deuteriochloroform with tetramethylsilane as an internal standard. Infrared spectra (film or KBr pellet) were recorded using a Perkin-Elmer Model 421 or Model 237B spectrophotometer; ultraviolet spectra were measured with a Cary Model 14 recording spectrophotometer. Combustion analyses were performed in the microanalytical laboratory at Stanford University.

2-Indanone (IX).—Using the method of Horan and Schiessler,[18] 2-indanone was prepared from indene in 58–62% yield. The ketone melted at 55–56.5° (lit.[18] mp 57–58°).

cis-**2-Hydrindanone (X).**—A solution of 2-indanone (IX, 10.0 g, 0.0755 mole) in 300 ml of absolute ethanol was hydrogenated over 0.5 g of ruthenium dioxide (Engelhard, 59% ruthenium dioxide) at 50° and 1500 psi for 24 hr. After removal of the catalyst and solvent, the crude product was dissolved in 100 ml of acetone and titrated with 8 N chromic acid solution while being cooled in an ice bath. The solution was neutralized with sodium bicarbonate (5%, 35 ml), and 94 ml of solvent was removed by distillation. The residue was extracted with three 50-ml portions of ether. After drying the ether solution, distillation gave the pure ketone as a colorless liquid, bp 108–110° (23 mm), n^{20}D 1.4828 [lit.[30] bp 109° (23 mm), $n^{16.7}$D 1.4846]. The over-all yield of X was 44%. The semicarbazone was prepared and recrystallized from 95% ethanol (75% yield). It melted at 207–208° dec (213–214° cor). Reported values are 215–216,[30] 215,[31a] and 212–213°.[31b]

2-Indanol (XI).—To a stirred slurry of lithium aluminum hydride (5.86 g, 0.155 mole) in 100 ml of anhydrous ether was added a solution of 2-indanone (IX, 20.0 g, 0.152 mole) in 250 ml of ether. After stirring for 1 hr, the reaction mixture was decomposed with saturated, aqueous sodium sulfate and filtered. Evaporation of ether from the dry (magnesium sulfate) solution gave 18.9 g (90%) of 2-indanol melting at 68–70° (lit.[32] mp 68–9.5°). The phenylurethan was prepared and crystallized twice from ethyl acetate. It melted at 128–131° (lit.[32] mp 130°).

4,5,6,7-Tetrahydro-2-indanol (XII).—While maintaining a dry nitrogen atmosphere, freshly distilled *n*-propylamine (130 ml) was added to a mixture of 2-indanol (XI, 5.32 g, 0.0396 mole) and 2.88 g (0.415 g-atom) of lithium cut into small pieces. The mixture was stirred for 15 min in an ice bath followed by 24 hr standing at room temperature. Solid ammonium chloride was cautiously added (cooling) until the mixture was a milky, off-white color and further addition caused no further evolution of heat. Water (200 ml) and ether (200 ml) were added and the layers were separated. The aqueous layer was shaken with three 100-ml portions of ether, and the combined ether solution was dried over magnesium sulfate. Evaporation of solvent followed by distillation of the residue gave 4.61 g (85%) of XII as a colorless oil, bp 83° (5 mm), which crystallized in the receiver. The analytical sample was prepared by crystallization from petroleum ether (bp 77–110°) followed by sublimation. It melted at 53.0–55.5°. The product decolorized bromine in carbon tetrachloride and gave a yellow color with tetranitromethane; the ultraviolet spectrum showed only end absorption and the infrared spectrum indicated the absence of vinyl hydrogen atoms.

Anal. Calcd for C₉H₁₄O: C, 78.21; H, 10.21. Found: C, 77.94; H, 10.15.

When an attempt was made to prepare XII by direct reduction of 2-indanone (13.2 g, 0.100 mole) with lithium (6.13 g, 0.0885 g-atom) in *n*-propylamine (250 ml) by the procedure described above, the alcohol was obtained in only 9% yield.

Tricyclo[4.3.1.0¹,⁶]decan-8-ol (XIII).—Zinc–copper couple was prepared as described Shank and Schecter.[33] To a stirred slurry of zinc–copper couple (8.15 g, 0.125 mole, of zinc) in anhydrous ether (100 ml) in a 500-ml flask fitted with a reflux condenser topped by a calcium chloride tube were added diiodomethane

(30) W. Hückel and H. Friedrich, *Ann.*, **451**, 132 (1927).

(31) (a) A. K. Kandiah, *J. Chem. Soc.*, 922 (1931); (b) R. L. Augustine and A. D. Broom, *J. Org. Chem.*, **25**, 802 (1960).

(32) W. Hückel and F. J. Bollig, *Ber.*, **86**, 1137 (1953).

(33) R. S. Shank and H. Schecter, *J. Org. Chem.*, **24**, 1825 (1959).

(26.8 g, 0.100 mole) and iodine (0.15 g). The mixture was refluxed for 30 min. Heating was discontinued and a solution of 4,5,6,7-tetrahydro-2-indanol (XII, 10.0 g, 0.0723 mole) in 65 ml of ether was added during 30 min. After refluxing the mixture for 26.3 hr, 2-methyl-2-butene (5.0 g, 0.071 mole) was added, and heating was continued for an additional 17 hr. The cooled mixture was filtered through Supercel; the filter pad was thoroughly washed with ether, and the washings were added to the filtrate. The ether solution was extracted with hydrochloric acid (5%, 3 × 50 ml), sodium bicarbonate (5%, 3 × 50 ml), and brine (50 ml). The aqueous layers were extracted with ether and the combined ether solution was dried over magnesium sulfate. Removal of solvent and distillation of the residue gave 9.32 g of a pale yellow oil which was found (tlc) to be a mixture of starting material and product.

The reaction was repeated using the above product in 25 ml of ether and the following amounts of reagents: zinc–copper couple (11.8 g, 0.181 mole, of zinc) in 100 ml of ether, iodine (0.15 g), diiodomethane (32.1 g, 0.120 mole), and 2-methyl-2-butene (8.5 g, 0.12 mole). The durations of the three reflux periods were 90 min, 22 hr, and 21 hr, respectively. Distillation of the product gave 4.57 g (42%) of a colorless oil, bp 104–106° (11 mm), which crystallized in the receiver. After two crystallizations from pentane at −70°, the alcohol XIII melted at 61–68°: ν_{max}^{KBr} 3068, 2998 (cyclopropane), and 1041 cm^{-1} (C–O).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.48; H, 10.50.

Tricyclo[4.3.1.0^{1,6}]decan-8-one (XIV).—Chromium trioxide–pyridine complex was prepared from 16.5 g (0.165 mole) of chromium trioxide and 165 ml of pyridine as described by Poos, *et al.*[34] To this stirred slurry was added a solution of alcohol XIII (5.65 g, 0.0371 mole) in 55 ml of pyridine. After stirring the mixture for 25 hr, water (200 ml) was added, and it was extracted with ether (one 200- and four 100-ml protions). The combined ether solution was shaken in series with water (50 ml), sulfuric acid (1.8 *M*, 8 × 25 ml), water (30 ml), sodium bicarbonate (5%, 25 ml), and water (25 ml). After drying (magnesium sulfate) the solution and evaporation of ether, distillation of the residue gave 4.00 g (72%) of ketone XIV as a colorless oil, bp 92–100° (13 mm), which was shown by glpc to be *ca.* 98% pure. The pure ketone was isolated by preparative glpc (1 in. × 6 ft column of 20% Carbowax 20 M on 60–80 mesh firebrick at 206° with a helium flow rate of 300 cc/min) followed by distillation, bp 96° (12 mm). The infrared spectrum indicated the presence of a cyclopropane ring (3045 and 2975 cm^{-1}) and a cyclopentanone (1742 cm^{-1}).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.92; H, 9.24.

10-Oxatricyclo[4.3.1.0^{1,6}]decan-8-one (XVI).—To a stirred solution of 5.12 g (0.0370 mole) of 4,5,6,7-tetrahydro-2-indanol (XII) in 50 ml of dry ether was added 83 ml of a ether solution containing 0.111 equiv of monoperphthalic acid. After an initial exothermic reaction which lasted for *ca.* 3 min, the flask was stoppered and stirring was continued for 5.25 hr at 4°. The reaction mixture was filtered, and the ether solution was shaken with sodium bicarbonate (three 25-ml portions) and dried over magnesium sulfate. Removal of ether under reduced pressure gave 5.10 g of a colorless oil (XV).

Without further purification, 1.02 g (0.00658 mole) of the epoxy alcohol XV in 10 ml of pyridine was added to a stirred slurry of chromium trioxide–pyridine complex prepared from 3.0 g of chromium trioxide and 30 ml of pyridine. After stirring for 24 hr, the reaction mixture was worked up as described above for the preparation of ketone XIV. The product (XVI) was isolated by distillation as a colorless oil (0.20 g, 20%) having bp 48–50° (25 μ), n^{20}D 1.4842. The infrared spectrum indicated the presence of a cyclopentanone (1748 cm^{-1}) and a fully substituted epoxide ring.

Anal. Calcd for $C_9H_{12}O_2O_2$: C, 71.02; H, 7.95. Found: C, 71.35; H, 8.16.

If purification of XVI was attempted by distillation at aspirator pressure or tlc on silica gel G, partial isomerization to an unsaturated hydroxy ketone occurred. A small amount of the isomerization product (XVII) was isolated by preparative tlc on silica gel G, using 3:2 ether–benzene, as a crystalline solid, mp 99–100°.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.97; H, 7.84.

β-Napthyl Methyl Ether (XIX).—β-Napthol (Eastman technical grade) was methylated with sulfuric acid and methanol in 56% yield by the procedure of Stork.[19] The β-naphthyl methyl ether melted at 71.5–72.2° (lit.[19] mp 71–72°).

β-Tetralone (XX).—β-Tetralone was prepared in 42.5% yield by the procedure of Soffer, *et al.*,[20] except that the reduction was carried out on β-naphthyl methyl ether (the ethyl ether was employed in the reference cited.). The product had bp 91–94° (5 mm) and n^{20}D 1.5597 [lit.[20] bp 92–94° (1.8 mm), n^{20}D 1.5594].

β-Tetralol (XXI).—To a stirred slurry of lithium aluminum hydride (5.69 g, 0.150 mole) in 225 ml of ether was added during 50 min a solution of β-tetralone (XX, 21.1 g, 0.144 mole) in 250 ml of ether. After stirring for 3 hr, hydrochloric acid (3 *N*, 200 ml) was cautiously added (cooling). The ether layer was separated, and the aqueous layer was extracted with 100 ml of ether. The combined ether solution was shaken with sodium bicarbonate (5%, 30 ml) and water (30 ml) and dried over sodium sulfate. Removal of ether and distillation of the residue gave 17.7 g (80%) of β-tetralol (XXI) as a viscous, colorless oil having bp 133–135° (12 mm), n^{19}D 1.5623 [lit. bp 139–140° (12 mm),[31] n^{25}D 1.5625[36]].

1,2,3,4,5,6,7,8-Octahydro-2-naphthol (XXII).—While maintaining a dry nitrogen atmosphere, 5.60 g (0.808 mole) of lithium in the form of small pieces was added to a solution of β-tetralol (XXI, 12.0 g, 0.081 mole) in 210 ml of ethylamine–*n*-propylamine (1:2 by volume). The mixture was cooled in an ice bath and stirring was commenced. After 4 hr the excess lithium was mechanically removed, and solid ammonium chloride was cautiously added until further addition caused no further evolution of heat. The reaction mixture was worked up as described for the preparation of alcohol XII. The product (XXII) was isolated by distillation (9.63 g, 78%) as a viscous, very pale yellow oil having bp 83–88° (4 mm), n^{19}D 1.5220. The product decolorized bromine in carbon tetrachloride, and the infrared spectrum indicated the presence of a hydroxyl group (3320 and 1042 cm^{-1}) and a double bond (*ca.* 1650 cm^{-1}) lacking vinyl hydrogen atoms. The ultraviolet spectrum indicated the presence of *ca.* 5% of XXI as an impurity.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.51; H, 10.36.

Tricyclo[4.4.1.0^{1,6}]undecan-3-ol (XXIII).—The reaction was carried out essentially as described above for the preparation of alcohol XIII using the following amounts of reagents: zinc–copper couple (16.3 g, 0.250 mole, of zinc) in 165 ml of ether, iodine (0.15 g), diiodomethane (16.1 ml, 53.5 g, 0.202 mole), alcohol XXII (8.60 g, 0.0564 mole) in 25 ml of ether, and 20.0 g (0.244 mole) of cyclohexene (in place of the 2-methyl-2-butene). The durations of the three reflux periods were 40 min, 45 hr, and 25 hr, respectively. The product (XXIII) was isolated by distillation as a colorless liquid: fraction 1, bp 81–87° (3.5 mm), n^{19}D 1.5076 (2.37 g); fraction 2, bp 94–95° (3.5 mm), n^{19}D 1.5118 (3.29 g); total, 5.66 g (61%). The product did not decolorize bromine in carbon tetrachloride, and the infrared spectrum indicated the presence of a hydroxyl group (3320 and 1050 cm^{-1}) and a cyclopropane ring (3045 cm^{-1}).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.02; H, 10.84 (sample from fraction 1).

Tricyclo[4.4.1.0^{1,6}]undecan-8-one (XXIV).—A solution of 5.18 g (0.0312 mole) of the tricyclic alcohol XXIII in 50 ml of pyridine was added to a stirred slurry of chromium trioxide–pyridine complex prepared from 12.5 g (0.125 mole) of chromium trioxide and 125 ml of pyridine. After stirring for 24 hr, the reaction mixture was worked up as described above for the preparation of ketone XIV. Distillation gave 2.86 g (56%) of a colorless oil having bp 65–70° (4.5 mm), which was shown by glpc to consist of a major component (80%) and at least six impurities. The pure ketone (XXIV) was isolated by preparative glpc (1 in. × 6 ft column of 20% Carbowax 20 M on 60–80 mesh firebrick at 195° with a helium flow rate of 300 cc/min) followed by distillation: bp 55–57° (3.5 mm), n^{11}D 1.5008. The infrared spectrum of XXIV indicated the presence of a carbonyl group (1711 cm^{-1}) and a cyclopropane ring (3050 and 2995 cm^{-1}), and the ultraviolet spectrum indicated the presence of a saturated ketone [λ_{max}^{EtOH} 289 mμ (ϵ 77)]. Final confirmation of structure XXIV

(34) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(35) F. Straus and A. Rohrbacher, *Ber.*, **54**, 55 (1921).

(36) W. A. Svirbely, W. M. Eareckson III, K. Matsuda, H. B. Pickard, I. S. Solet, and W. B. Tuemmler, *J. Am. Chem. Soc.*, **71**, 507 (1949).

came from the pmr spectrum: the cyclopropane hydrogens appeared as an AB pattern; the two doublets (one proton each) were centered at δ 0.44 and 0.53 (J = 9.0 cps); the two protons between the cyclopropane ring and the carbonyl group also appeared as an AB pattern with the two doublets centered at δ 2.36 and 2.66 (J = 17.6 cps); at 60 Mc the two center lines of this AB pattern were coincident, but at 100 Mc they split into the expected four-line pattern. The total integral was in accord with structure XXIV.

Anal. Calcd for $C_{11}H_{15}O$: C, 80.44; H, 9.82. Found: C, 80.02; H, 9.82.

1,1,3,3-Tetramethyl-2-indanone (XXV).—To a stirred solution of 2-indanone (IX, 10.0 g, 0.0757 mole) in 160 ml of dry (potassium carbonate), redistilled (bp 81.3–82.0°) *t*-butyl alcohol was added during a few seconds a solution of potassium (17.6 g, 0.454 mole) in *t*-butyl alcohol (300 ml). *Immediately*, methyl iodide (56.5 ml, 129 g, 0.908 mole) in 60 ml of *t*-butyl alcohol was added during a few seconds. The reaction mixture was cooled in an ice bath for the first 2 min and then heated under reflux during 2.5 hr. In the course of the first 15 min of the reflux period an additional 15.0 ml (34.2 g, 0.241 mole) of methyl iodide was added dropwise. After cooling, the product was poured into water (0.5 l.), and 200 ml of chloroform was added. The layers were separated and the aqueous layer was extracted with an additional 100 ml of chloroform. The combined organic solution was shaken with hydrochloric acid (5%, 70 ml) and water (70 ml), dried over magnesium sulfate, and concentrated to a small volume using a rotary evaporator. Water (150 ml) and a few crystals of sodium thiosulfate pentahydrate were added to the dark red oil, steam was introduced, and the product was distilled. The product crystallized in the ice-cooled receiver. The crystals were removed by filtration, covered with a rubber dam, sucked on the filter for 1 hr, and dried at reduced pressure for 12 hr over anhydrous calcium chloride. The yield was 10.1 g (71%). The analytical sample of ketone XXV was prepared by sublimation and melted at 75.0–76.5°: λ_{max}^{EtOH} 252 (sh), 259, 265, 272, and *ca.* 295 (sh) mμ (ϵ_{max} 344, 685, 1150, 1340, and 19.6 respectively); ν_{max}^{KBr} 3000–3100 (several), 1630 (br), 1478, 759 and 751 (doublet) (indan derivative), 1738 (C=O), 1377, and 1354 cm^{-1} (*gem*-dimethyl). The pmr spectrum of XXV consisted of two singlets at δ 1.32 and 7.23 having areas in the expected ratio of 3:1.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.08; H, 8.62.

1,1,3,3-Tetramethyl-*cis*-2-hydrindanone (XXVI).—A solution of 10.0 g (0.053 mole) of ketone XXV in 300 ml of absolute ethanol containing 0.50 g of ruthenium dioxide (Engelhard) was shaken at 50–70° in a high-pressure bomb with hydrogen at 1500 psi. After 21 hr the bomb was opened and the catalyst was removed by filtration. The ketone (XXVI) was isolated by distillation through a spinning-band column: fraction 1, bp 105–106° (5 mm), $n^{20}D$ 1.4794 (0.47 g); fraction 2, bp 106° (5 mm), $n^{20}D$ 1.4800 (4.78 g); total, 5.99 g (51% yield). Fractions 1 and 2 were shown by glpc (Carbowax column at 161°) to be 95 and 98% pure, respectively. The analytical and spectral determinations and subsequent photolyses were carried out on fraction 2. The compound did not decolorize bromine in carbon tetrachloride, and the ultraviolet spectrum indicated the presence of a saturated ketone: $\lambda_{max}^{C_8H_{12}}$ 265 (sh), 273, 300, 310, and 321 (sh) mμ (ϵ 7.4, 9.9, 16.8, 15.9, and 9.3, respectively). The infrared spectrum [1727 (C=O), 1360, and 1380 cm^{-1} (*gem*-dimethyl)] was also in accord with the assigned structure. The pmr spectrum of XXVI consisted of two singlets at δ 1.02 and 1.07 due to the methyl protons, a band at δ 1.50 due to the methylene protons, and a band at δ 2.05 due to the methine protons. Areas under the absorption bands were in accord with assignments given.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41; Found: C, 80.44; H, 11.69.

1,1,3,3-Tetramethyl-2-indanol (XXVII).—To a stirred slurry of lithium aluminum hydride (2.30 g, 0.0606 mole) in 100 ml of anhydrous ether was added a solution of ketone XXV (9.11 g, 0.0484 mole) in 125 ml of ether. After stirring for 3 hr, hydrochloric acid (3 N, 100 ml) was added and the mixture was worked up as described above for the preparation of β-tetralol. Evaporation of ether gave XXVII as a white crystalline solid which was dried over anhydrous calcium chloride at room temperature and reduced pressure for 14 hr. The product weighed 9.62 g (104% yield) and was shown by tlc to be contaminated by a small amount of mineral oil, apparently introduced by the stirrer. The analytical sample was purified by sublimation and melted at

85.0–85.5°: λ_{max}^{EtOH} 251 (sh), 257, 263.5, and 270.5 mμ (ϵ_{max} 340, 650, 1080, and 1230, respectively); ν_{max}^{KB} 3400 (OH), 3000–3055 (several), 1630, 1585 (w), 1483, 765 and 750 (doublet) (indan derivative), 1380, 1365 (*gem*-dimethyl), and 1060 cm^{-1} (C–O).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.76; H, 9.37.

1,1,3,3-Tetramethyl-4,5,6,7-tetrahydro-2-indanol (XXIX).—The reduction of 1,1,3,3-tetramethyl-2-indanol (XXVII, 9.49 g, 0.0498 mole) with lithium (3.55 g, 0.511 g-atom) in *n*-propylamine (150 ml) was carried out as described above for the preparation of alcohol XII; the reaction time was 24 hr. The product, which was isolated by distillation, was shown by tlc and ultraviolet spectroscopy to consist of 92% of unreacted starting material and 8% of product. This mixture was reduced a second time, and the product (4.13 g) still contained *ca.* 50% of unreacted XXVII. This mixture was dissolved in 30 ml of anhydrous ether, and 5.0 ml of freshly distilled acetyl chloride was added. After refluxing for 22 hr, the solution was cooled, and 5 ml of 5% sodium bicarbonate was added. The ether layer was separated and shaken with sodium bicarbonate (5%, four 5-ml portions) and water (5 ml). Evaporation of ether from the dry (magnesium sulfate) solution gave 3.80 g of the desired mixture of acetates (ν_{max}^{film} 1740, 1369, 1236, and 1047 cm^{-1}).

This acetate mixture was reduced as before with 3.50 g of lithium and 150 ml of *n*-propylamine for 28 hr. By steam distillation there was isolated 1.67 g of a white crystalline solid, which was shown by infrared and ultraviolet spectroscopy to consist of a mixture of alcohols containing 24% of the original starting material (XXVII).

The alcohol mixture was dissolved in 25 ml of acetone and titrated with 8 N chromic acid solution. Sodium bicarbonate (5%, 10 ml) and water (20 ml) were added, and 23 ml of solvent was removed by distillation. The product was isolated as a pale yellow oil (1.37 g) by extracting with ether (three 50-ml portions), drying the ether solution (magnesium sulfate), and evaporating the ether. By preparative glpc on a 1 in. × 6 ft column of 20% Carbowax 20 M on 60–80 mesh firebrick at 160° with a helium flow rate of 300 cc/min, there was isolated 0.24 g of 1,1,3,3-tetramethyl-2-indanone (XXV) and 0.59 g (6% yield from XXVII) of the desired ketone (XXIX), mp 29–30°. Ketone XXIX decolorized bromine in carbon tetrachloride without evolution of hydrogen bromide, and the infrared spectrum indicated the presence of a nonconjugated cyclopentenone grouping (1736 cm^{-1}), a *gem*-dimethyl group (1372 and 1350 cm^{-1}), and a double bond lacking vinyl hydrogen atoms. The ultraviolet spectrum of XXIX in ethanol [λ_{max} 295 mμ (ϵ 16.5)] indicated a nonconjugated ketone and exhibited a second absorption band at 234 mμ (ϵ 290) probably due to a little undetected impurity.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.93; H, 10.59.

2-Methylcyclohexanone.—Oxidation of 2-methylcyclohexanol (Eastman, practical grade) in benzene with aqueous, acidic sodium dichromate[22] gave a 69% yield of 2-methylcyclohexanone, bp 163–164°, $n^{18}D$ 1.4479 [lit.[22] bp 162.5–3.5° (742 mm), $n^{25}D$ 1.4459].

2,2,6,6-Tetramethylcyclohexanone (XXVIII).—The procedure employed was similar to that described by Fischer and Wunderlich.[23] To a stirred slurry of sodamide (27.0 g, 0.692 mole) in 350 ml of anhydrous ether in a 1 l. flask fitted with an efficient reflux condenser topped by a soda lime tube was added (during 25 min) 75.3 g (0.671 mole) of 2-methylcyclohexanone. After refluxing for an additional 2 hr, 200 ml of water was cautiously added to the cooled solution. The aqueous layer was separated and extracted with ether (two 100-ml portions). The combined ether solution was shaken with sulfuric acid (10%, 50 ml) and sodium carbonate (10%, 50 ml), and was dried over sodium sulfate. Fractionation through a 20-cm Vigreux column gave 72.4 g of a colorless oil, bp 168–171°.

Essentially this same procedure was repeated four more times, in each case employing the product from the preceding methylation. Distillation after the fifth methylation gave four fractions as colorless liquids: fraction 1, 5.73 g, bp 183–184°, $n^{21}D$ 1.4459; fraction 2, 17.5 g, bp 184.0–185.0°, $n^{21}D$ 1.4468; fraction 3, 29.0 g, bp 185.0–185.1°, $n^{1}D$ 1.4469; and fraction 4, 4.50 g, bp 185.1°, $n^{21}D$ 1.4471. The over-all yield of pure 2,2,6,6-tetramethylcyclohexanone (fractions 2–4) was 49.3%. Its reported[37] physical constants are bp 185° and $n^{20}D$ 1.4470.

(37) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

TABLE II

Ketone (g)	Solvent (ml)	Time, hr	Gas,[a] % theory	Products[b] (peak area %)
XIV (0.564)	Cyclohexane (5.0)	12.25	68	XXX (70), XIV (30)
XIV (0.564)	Benzene (5.0)	9.6	88	XXX (100)
XXIV (0.280)	Cyclohexane (5.0)	10.1	22	XXX (13), XXXI (28), (6), (26), (9), (9)
XXV (0.297)	Cyclohexane (5.0)	5.5	88	XXXII (91), (1), (3), (<1), XXV (5)
XXV (0.262)	Cyclohexene (5.0)	7.1	93	XXXII (81), (5), (2), (7), XXV (5)
XXV (0.252)	Tetrahydrofuran-d_8 (10.9)	10.65	89	XXXII (78), (2), XXV (20)
XXV (0.310)	2-Propanol (5.0)	23	81[c]	XXXII (78), (3), XXV (13), (1), (3), XXVII (2)[d]
XXIX (0.271)	Cyclohexane (5.0)	4.9	98	XXXIII (55), XXXIV (45)
XXVI (0.321)	Cyclohexane (5.0)	23	91	XXXV (53), XXXVI (18), XXXVII (27), three others (2)
XXVI (0.214)	2-Propanol (5.0)	174	316[e]	XXXV, XXXVI, XXXVII, pinacol,[f] minor products
XXXVIII (0.299)	Cyclohexane (5.0)	25.5	77	(13), (15), XXXIX (51), (5), (11), (3), (2)
XVI (0.550)	Cyclohexane (5.0)	28.4	18[g]	XVI + several minor products
XVI (0.217)	Methanol (10.0)	2.6	16[g]	XVI + several minor products
X (0.289)	Cyclohexane (5.0)	22	12	X (100)

[a] Carbon monoxide unless otherwise noted.   [b] Listed in order of increasing glpc retention times on a Carbowax 20 M or SE 30 column; unidentified products are indicated only by peak area per cents.   [c] Carbon monoxide plus a trace of methane.   [d] Also, acetone and a product with retention time slightly shorter than acetone (peak areas, respectively, 8 and 4% of the area of the peak due to product XXXII) were present; acetone and XXVII were identified by comparison of glpc retention times with those of authentic samples.   [e] Carbon monoxide plus methane.   [f] Identified by infrared, ultraviolet, and pmr spectroscopy.   [g] Carbon monoxide plus carbon dioxide.

TABLE III

Ketone	Product (yield, %)[a]	Column temp, °C	Helium flow rate, cc/min	Retention time, min	Calcd % C	Calcd % H	Calcd Mol wt	Found % C	Found % H	Found Mol wt[b]
XIV	XXX	103	280	28	88.45	11.55		88.59	11.48	
XXIV	XXX (6)	122	240	37						
	XXXI (13)	122	240	56	88.16	11.84		88.10	11.70	
XXV	XXXII	158	315	14	89.94	10.06	160	89.76	9.92	175
XXIX	XXXIII (32)	114	300	22	87.73	12.27		87.40	12.25	
	XXXIV (25)	114	300	28	87.73	12.27		87.54	12.28	
XXVI	XXXV (32)	114	300	31	86.67	13.33	166	86.90	13.32	180
	XXXVI XXXVII } (20)[c]	114	300	41	86.67	13.33		86.62	13.42	
XXXVIII	XXXIX (8)	63	235	40	85.63	14.37		85.37	14.14	

[a] Isolated yield.   [b] Vapor pressure lowering.   [c] On reinjecting the mixture of XXXVI and XXXVII onto the glpc column at 73°, a broad peak was observed having a retention time of 3.3–5.2 hr; by collecting fractions as this peak was observed, it was possible to obtain a pure sample of XXXVII and a mixture enriched (ca. 2/3)in XXXVI.

Photolyses.—Purified solvents were used for all photolyses; cyclohexane was Matheson Coleman and Bell Spectroquality Reagent, and benzene was Eastman Spectro Grade; ultraviolet spectroscopy indicated that the cyclohexene contained ca. 7.6 × 10^{-1} g/l. of cyclohexadiene as an impurity; no acetone could be detected in the isopropyl alcohol employed either by gc or ultraviolet spectroscopy.

The photolyses were carried out with radiation provided by a Hanovia Model 30600, 100-w, high-pressure mercury arc. Samples were placed 5–6 cm from the arc and cooled by a fan directed at the sample but not at the arc. Samples were contained in a flat, circular quartz cell having a diameter of 81 mm, an internal thickness of ca. 6.5 mm, and a wall thickness of ca. 1.2 mm. Gas volumes were measured in a nitrogen-filled system using mercury-filled burets. The nitrogen atmosphere was established by alternately evacuating (aspirator) the system and filling it with prepurified nitrogen (at least ten cycles). The identities of the gaseous products reported were confirmed by observation of their characteristic infrared spectra.[38]

The photolyses are summarized in Table II, and the isolation of products by preparative glpc (1 in. × 6 ft column of 20% Carbowax 20M on 60–80 mesh firebrick) along with analytical results are listed in Table III.

Ozonolysis of 1,2-Diisopropylidinecyclohexane (XXXIV).—A solution of XXXIV (ca. 0.047 g) in ca. 1 ml of deuteriochloroform was diluted with an equal volume of dry methylene chloride and ozonized at −70° using the output of a Welsbach Ozonizer until the appearance of a blue color. The solution was flushed with nitrogen at −70°, after which the solvent was removed by distillation at reduced pressure. Water (2 ml) was added and the mixture was refluxed for 15 min. Sodium hydroxide (5%, 5 ml) was added, the mixture was steam distilled, and 1 ml of distillate was collected.

To the steam distillate were added 1 ml of 5% methanolic sulfuric acid, 3 drops of menthofuran,[39] and 2 ml of ethanol. After 18 hr at 3°, the crystals were collected, washed with 5 ml of cold, dilute aqueous methanol containing a trace of potassium hydroxide, and dried at reduced pressure over anhydrous calcium chloride. The total yield (two crops) of product was 0.016 g. The product melted at 83–88° (lit.[40] for the bismenthofuryl derivative of acetone, mp 88°) and gave a spot on a thin layer chromatogram (silica gel G, petroleum ether) with an R_f identical with that of an authentic sample[39] of the bismenthofuryl derivative of acetone.

The steam distillation residue described above was acidified with 6 ml of 5% hydrochloric acid, extracted with ether (two 20-ml portions), dried (magnesium sulfate), and freed from solvent. The colorless liquid thus obtained was dissolved in 2 ml of 95% ethanol. This solution was added to a solution of 0.125 g of 2,4-dinitrophenylhydrazine and 1 ml of concentrated sulfuric acid in 10 ml of 95% ethanol. The resulting solution was warmed on a steam bath for 10 min and then allowed to stand for 48 hr at 3°. The precipitate was collected, washed with cold methanol, and recrystallized from acetic anhydride. The red solid (0.005 g) had mp 217–219° dec (lit.[41] mp 218–219° for the red bis-2,4-dinitro-phenylhydrazone of 1,2-cyclohexanedione).

(38) R. H. Pierson, A. N. Fletcher, and E. S. Gantz, Anal. Chem., **28**, 1218 (1956).

(39) Kindly provided by J. M. Erickson.
(40) J. M. Erickson, Stanford University, unpublished results.
(41) H. Adkins and A. G. Rossow, J. Am. Chem. Soc., **71**, 3836 (1949).