(15%) of 1,2,3-triphenylnaphthalene, m.p. 151–152°, lit.[17] m.p. 152°. The residual material was largely deoxybenzoin, as shown by the infrared spectrum.

The mononitro derivative, prepared by nitration of 0.169

g. of the 1,2,3-triphenylnaphthalene with 0.1 ml. of concentrated nitric acid in 5 ml. of acetic acid (warmed 50 minutes on a steam-bath) melted at 210–203°, lit.[17] m.p. 200–201°. Reduction of this nitro compound by hydrogen (1 atm.) over palladium-on-charcoal yielded the monoamino derivative, m.p. 187–189°, lit.[17] m.p. 189–190°.

(17) L. E. Smith and H. H. Hoehn, THIS JOURNAL, 63, 1184 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KANS.]

Stereospecific Angular Alkylation. A New Application of the Claisen Rearrangement[1]

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Claisen rearrangement of vinyl ethers of suitably constituted polycyclic allylic alcohols is shown to provide a new, stereospecific method for the introduction of an angular substituent into polycyclic systems. Model studies with Δ^2-cyclohexenol and 3-methyl-Δ^2-cyclohexenol are described, and applications of the sequence to $\Delta^{9(10)}$-1-octalol and the epimeric Δ^4-cholestene-3-ols are reported.

Despite the fact that various effective methods have been devised for the synthesis of angularly substituted polycyclic systems,[2] there is continued interest in the development of still other means for this purpose, especially ones which are completely or at least highly stereoselective. By virtue of its intramolecular character, the Claisen-type rearrangement of allyl vinyl ethers (A)[3] and of allyl acetoacetates (B)[4] appeared to us to offer the possibility of being applicable as a new and potentially
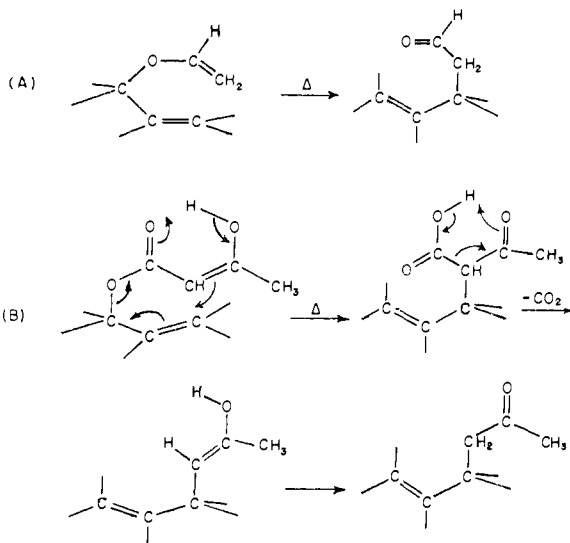
useful method for the stereoselective introduction of an angular functional group into a suitably constituted ring structure. This stereospecificity is such that, if the allylic group is contained in a ring, the new carbon–carbon bond which is formed in the

reaction will necessarily be *cis* to the carbon–oxygen bond that undergoes cleavage. In this report we present results of an exploratory investigation into such an extension of these rearrangements.

Model Studies.—Except for the phenyl ether of Δ^2-cyclohexenol,[5] substances in which the participating allylic group is incorporated into a ring apparently have not been examined previously in the Claisen or Cope rearrangement. Thus, although Claisen in his original memoir[6] disclosed the rearrangement of 3-allyloxymethylenecamphor (I) to the C-allyl derivative II,[7] and, more recently,
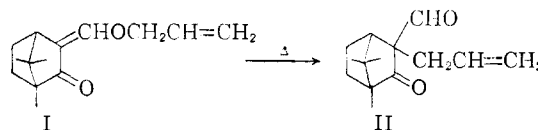
Brannock[8] has reported three additional examples of a similar nature, vinyl ethers or acetoacetic esters of cyclic allylic alcohols do not appear to have been prepared or studied previously. Accordingly, as a basis for possible extensions to bicyclic and larger ring systems, preliminary investigations were undertaken with these derivatives of Δ^2-cyclohexenol and 3-methyl-Δ^2-cyclohexenol.

The Δ^2-cyclohexenol used in this work was prepared by hydrolysis of 3-bromocyclohexene, which, in turn, was obtained directly from cyclohexene by the Wohl–Ziegler method with N-bromosuccinimide.[9] 3-Methyl-Δ^2-cyclohexenol[10] was prepared by carefully controlled borohydride reduction of

(1) From the Ph.D. Thesis of Ivan C. Nordin, The University of Kansas, 1960. A preliminary report of this work appeared as a Communication to the Editor, THIS JOURNAL, 81, 3151 (1959). A portion of it was also presented before the Division of Organic Chemistry at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 13–18, 1959.

(2) For leading references (in relation to the steroid field), see L. F. Fieser and M. Fieser, "Steroids," Reinhold Publ. Corp., New York, N. Y., 1959, particularly Chapters 15, 16 and 19.

(3) Reviewed by D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. 1.

(4) W. Kimel and A. C. Cope, THIS JOURNAL, 65, 1992 (1943), and later papers.

(5) J. W. Cornforth, C. K. Hughes and F. Lions, J. Proc. Royal Soc. N. S. Wales, 71, 323 (1938) [C. A., 33, 148 (1939)].

(6) L. Claisen, Ber., 45, 3157 (1912).

(7) Experimental details of this work do not appear ever to have been published. Out of interest in the degree to which this particular rearrangement is stereospecific, we have prepared the dl-form of I and have found that its rearrangement at 220° leads, in excellent yield, to a mixture of the two possible stereoisomers of II. One of these, formed to a slightly greater extent than the other, is crystalline (m.p. 51–53°) and is readily separated from the second, which is a liquid. The fact that both possible stereoisomers of II are formed, and in comparable amounts, indicates that in a system of this type steric requirements for the rearrangement are practically non-selective.

(8) K. C. Brannock, THIS JOURNAL, 81, 3379 (1959).

(9) K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, Ann., 551, 80 (1942); cf. H. J. Dauben, Jr., and L. L. McCoy, THIS JOURNAL, 81, 4863 (1959).

(10) M. I. Bowman, C. C. Ketterer and G. Dinga, J. Org. Chem., 17, 563 (1952).

3-methyl-Δ^2-cyclohexenone. The latter was synthesized by means of the improved ethyl acetoacetate–formaldehyde condensation sequence described by Cronyn and Riesser.[11]

Reaction of these alcohols with diketene in the presence of pyridine as a catalyst[12] provided a convenient source of the corresponding acetoacetates IIIa and IIIb. The latter, on being heated to 175° or higher, with or without various recommended[13] "catalysts," underwent decomposition,

IIIa, R = H   IVa, R = H
IIIb, R = CH₂   IVb, R = CH₃
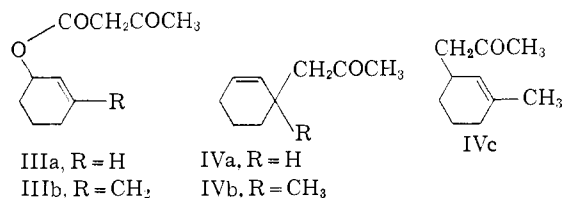
but not appreciably in the manner desired. Although the evolution of carbon dioxide was nearly quantitative, the predominant course of the reaction was elimination rather than rearrangement, with acetone and the respective conjugated dienes, 1,3-cyclohexadiene and mixed 1- and 2-methyl-1,3-cyclohexadiene and 3-methylenecyclohexene, being the major organic products formed. Only minor amounts of what were shown to be the corresponding cyclohexenylacetones IVa, IVb and IVc were produced. By catalytic hydrogenation IVa was converted into a saturated methyl ketone, the melting point of whose semicarbazone was in agreement with that recorded[14] for the semicarbazone of cyclohexylacetone. Vapor phase chromatographic comparison of authentic samples of 1-methyl-[15] and 3-methylcyclohexylacetone[16] with the dihydro derivative of the IIIb-pyrolysis product indicated that the latter, even after regeneration from the semicarbazone, was a mixture of IVb and IVc. The formation of IVc can be accounted for by an allylic ester rearrangement of IIIb taking place prior to alkylation and decarboxylation.[4]

In view of the fact that substituted acyclic allyl-acetones have frequently been obtained in good yield from the pyrolysis of the corresponding acetoacetic esters,[4] the extensive elimination observed in the preceding experiments is somewhat surprising. On the other hand, the report[5] that even the phenyl ether of Δ^2-cyclohexenol gives rearrangement products in only 20% yield, plus phenol and cyclohexadiene in 50–60% yield, suggests that an oxygenated allylic function in a cyclic system is perhaps more susceptible to elimination than it is in an acyclic one.[17] The possibility, however, that cyclic allyl vinyl ethers

might undergo rearrangement in preference to elimination is not excluded by this evidence. Indeed, as has been observed in these laboratories,[18] there is a comparatively small tendency for elimination to occur in the rearrangement of vinyl ethers of substituted open-chain allylic alcohols to the corresponding allylacetaldehydes.[19] In addition, such derivatives possess a further advantage over acetoacetic esters in that they are less liable to isomerization of the allylic function prior to rearrangement. Consequently, as a pattern for intramolecular angular alkylation in polycyclic systems, rearrangement of the cyclohexenyl vinyl ethers Va and Vb to the unsaturated aldehydes VIa and VIb, respectively, appeared to hold considerable promise.

Va, R = H   VIa, R = H
Vb, R = CH₃   VIb, R = CH₃
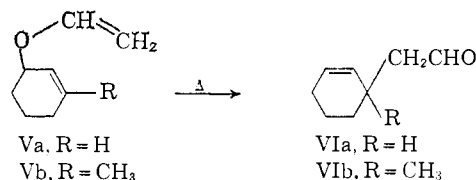
Although direct vinylation of allyl alcohol by the Reppe procedure[20] with pressurized acetylene at 90–95° has been reported[21] to give allyl vinyl ether in 71% yield, the synthesis of Va or Vb in this manner did not prove feasible. At the lowest temperature at which uptake of acetylene could be observed (150–160°), rearrangement to products susceptible to further reaction apparently took place. Application of the low-temperature mercuric sulfate-catalyzed vinyl exchange reaction of vinyl acetate with alcohols reported by Adelman[22] was also entirely unfruitful. However, the recently described mercuric acetate-catalyzed vinyl transetherification reaction of alkyl vinyl ethers with alcohols[23] did prove fairly satisfactory, and by this means the purified vinyl ethers Va and Vb could be prepared in yields of 35 to 40% by vinylation of the corresponding cyclohexenols with ethyl vinyl ether.

In contrast to the behavior of the acetoacetic esters IIIa and IIIb, the vinyl ethers Va and Vb rearranged cleanly when heated to 190–195°, furnishing the unsaturated aldehydes VIa and VIb, respectively, in yields of 90 to 95%. Only insignificant amounts of elimination products were observed. Hydrogenation of the rearrangement products afforded the known saturated aldehydes, cyclohexylacetaldehyde[24] and 1-methylcyclohexyl-

(11) M. W. Cronyn and G. H. Riesser, THIS JOURNAL, 75, 1664 (1953).

(12) Cf. W. Kimel, N. W. Sax, S. Kaiser, G. G. Eichmann, G. O. Chase and A. Ofner, J. Org. Chem., 23, 153 (1958); see also ref. 4.

(13) Cf. W. M. Lauer and E. I. Kilburn, THIS JOURNAL, 59, 2586 (1937), and L. Claisen and E. Tietze, Ber., 59, 2344 (1926); see also ref. 12.

(14) O. Wallach, Ann., 397, 196 (1913).

(15) For preparation see Experimental.

(16) A. Darzens and H. Rast, Compt. rend., 153, 772 (1913); cf. O. Wallach, Nachr. kgl. Ges. Wiss. Göttingen, 442 (1912) [C. A., 7, 486 (1913)].

(17) See p. 14 of ref. 3.

(18) A. W. Burgstahler, THIS JOURNAL, 82, 4681 (1960).

(19) Similar results have also been noted recently in a parallel investigation of the stereochemistry of the o-Claisen rearrangement of the phenyl ethers of such alcohols [E. N. Marvell and J. L. Stephenson, J. Org. Chem., 25, 676 (1960)].

(20) Cf. J. W. Copenhaver and N. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, N. Y., 1949.

(21) R. Paul, G. Roy, M. Fluchaire and G. Collardeau, Bull. soc. chim. France, 121 (1950).

(22) R. L. Adelman, THIS JOURNAL, 75, 2678 (1953); 77, 1669 (1955).

(23) W. H. Watanabe and L. E. Conlon, ibid., 79, 2828 (1957). In our experience the purity of the mercuric acetate is extremely critical (see Experimental).

(24) O. Wallach, Ann., 359, 313 (1908); see also refs. 43–46 below.

acetaldehyde.[25] Conversion of the corresponding acids VIIa[26] and VIIb to the δ-iodo-γ-lactones VIIIa[26,27] and VIIIb, respectively, provided additional evidence for the structures VIa and VIb assigned to the rearrangement products.

VIIa, R = H
VIIb, R = CH₃

VIIIa, R = H
VIIIb, R = CH₃
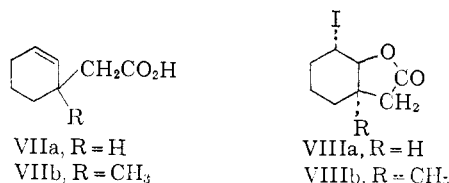
Polycyclic Applications.—With the finding that a quaternary center could be formed in a monocyclic model by the rearrangement Vb→VIb, suitable extensions of the method to polycyclic systems were in order. The first application of this type was to the bicyclic vinyl ether (IX) of $\Delta^{9(10)}$-1-octalol. This ether was prepared in 40% yield by the procedure of Watanabe and Conlon[23]

IX

CH₂CHO
X

XI
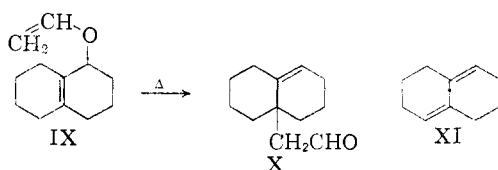
from $\Delta^{9(10)}$-1-octalol, which, in turn, was obtained by reduction of $\Delta^{9(10)}$-1-octalone[28] with lithium borohydride.

When heated in a sealed tube at 190-195° for 2 hr., IX afforded $\Delta^{4(10)}$-9-octalylacetaldehyde (X) in 75-80% yield, along with a small amount of dienic elimination product, e. g., XI.[29] In addition to assay and characterization by solid carbonyl derivatives, X was reduced over palladium-on-charcoal to furnish the corresponding saturated aldehyde, which in turn was oxidized by silver oxide to the known[30] cis-9-decalylacetic acid, m.p. 114-115°. The identity of the latter was further confirmed by degradation[30] to cis-9-decalincarboxylic acid, m. p. 121-122°.[30,31] Oxidation of the unsaturated aldehyde X with silver oxide afforded $\Delta^{4(10)}$-9-octalylacetic acid (XII), m.p. 103-106°, which was converted into the δ-iodo-γ-lactone XIV, m.p. 165-167.5° (infrared, 5.65 μ). Hydrogenation of XII gave largely cis-9-decalylacetic acid.

XII, R = CO₂H
XIII, R = CH₃

XIV
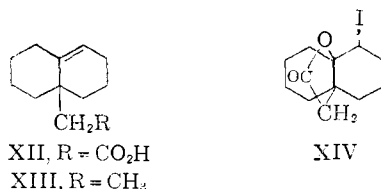
(25) L. Schmerling, THIS JOURNAL, 71, 698 (1949).

(26) E. E. van Tamelen and M. Shamma, ibid., 76, 2315 (1954).

(27) For a recent study of the mechanism and stereochemistry of the halolactonization reaction, see G. Berti, Tetrahedron, 4, 393 (1958).

(28) A. L. Wilds and N. A. Nelson, THIS JOURNAL, 75, 5360 (1953). For a more recent synthesis, cf. R. K. Hill and R. T. Conley, ibid., 82, 645 (1960).

(29) W. Hückel and U. Wörffel, Ber., 89, 2098 (1956).

(30) R. D. Haworth and A. F. Turner, J. Chem. Soc., 1240 (1958).

(31) W. G. Dauben and J. B. Rogan, THIS JOURNAL, 79, 5002 (1957). We are deeply grateful to Professor Dauben for sending us a comparison sample of this acid and also its trans isomer.

Since the somewhat variable stereochemical course of the hydrogenation of various substituted octalins appears to be controlled to a large extent by the nature of the angular substituent,[31,32] it was of interest to compare the results of the preceding reductions with the stereochemical outcome of the reduction of the corresponding 9-ethyl derivative XIII. The latter was readily obtained by Wolff-Kishner reduction of the semicarbazone of X and gave, by hydrogenation over palladium-on-charcoal, a mixture of cis- and trans-9-ethyldecalin. Gas chromatography indicated that the mixture consisted of about three parts of cis isomer to four parts of trans. For comparison, predominantly cis-9-ethyldecalin was similarly prepared by Wolff-Kishner reduction of the semicarbazone of the hydrogenation product of X that had given rise to cis-9-decalylacetic acid by oxidation.

In order to explore the potential utility of this new method of angular alkylation in a more complex system, we also examined the conversion of the vinyl ether (XV) of Δ^4-cholestene-3β-ol to Δ^3-5β-cholestenylacetaldehyde (5β-formylmethyl-Δ^3-cholestene, XVI). Reduction of cholestenone with lithium tri-t-butoxyaluminum hydride[33] at


XV

XVI, R = CHO
XVII, R = CO₂H
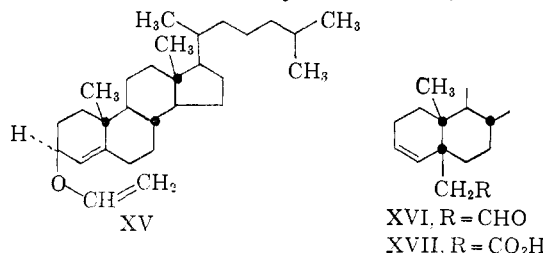
−40° gave nearly pure Δ^4-cholestene-3β-ol, practically free of the 3α-isomer. The crystalline vinyl ether XV, m.p. 56-57°, was obtained in 60-65% yield by the procedure already indicated,[23] and, on rearrangement in decalin or in dry, acid-free diglyme at 190-195° for several hours, afforded a crystalline, unsaturated aldehydic product formulated as XVI, m.p. 66-69°, in 80-85% yield. In the absence of solvent extensive side reactions occurred during heating. The infrared spectrum of the rearrangement product showed it to be a nonconjugated, unsaturated aldehyde containing a cis-disubstituted double bond. The n.m.r. spectrum[34] gave further support to this interpretation and also indicated that the aldehyde function was incorporated in a formylmethyl group attached to a quaternary carbon atom. In this connection, too, it should be noted that the corresponding dihydro acid XIX melts at 213-216°, thus clearly differentiating it from 3β-cholestanylacetic acid, m.p. 177°,[35] which is a conceivable alternative structure, if an allylic isomerization had taken place at some stage during the preparation or rearrangement of XV.

(32) L. S. Minckler, A. S. Hussey and R. H. Baker, ibid., 78, 1009 (1956).

(33) O. H. Wheeler and J. L. Mateos, Can. J. Chem., 36, 1431 (1958); cf. J. Fajkos, Collection Czechoslov. Chem. Communs., 24, 2284 (1959).

(34) We wish to express our appreciation to Dr. James N. Shoolery and his co-workers at the Varian Associates, Palo Alto, Calif., for making this determination.

(35) C. W. Shoppee and R. J. Stephenson, J. Chem. Soc., 2230 (1954).

XVIII, R = CHO
XIX, R = CO₂H
XX, R = CH₃

XXI

XXIII   XXIV
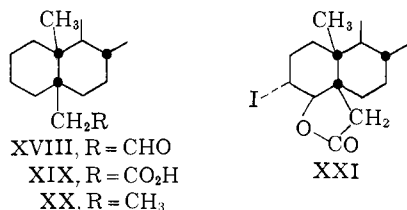
Reductive desulfurization of the ethylene thio-acetal derived from the dihydro aldehyde XVIII furnished 5β-ethylcholestane (XX), m.p. 67–69°. Apart from rearranged structures such as Westphalen's diol,[2] other 5-alkylated steroids which have been reported include 5α-methylated cholestanes,[36a] 5β-methylated pregnanes,[36b] and 5α-methylated androstanes.[36c]

Oxidation of the rearrangement product XVI with silver oxide at 65–70° provided the corresponding unsaturated acid XVII, m.p. 217–219°. This, by treatment with iodine–potassium iodide in weakly alkaline solution,[26] furnished a δ-iodo-γ-lactone, m.p. 230–231°, which is formulated as XXI. Since the iodolactonization reaction[26,27] almost certainly conforms to the generalized *trans* diaxial pattern of other ionic additions to flexible cyclohexene ring systems,[37] it is of interest that a pathway involving the quasi-chair conformation of ring A, which is observed ordinarily,[38] could not have been operative in the formation of this lactone. If it had been, the alternative γ-iodo-δ-lactone structure XXII would have been expected.
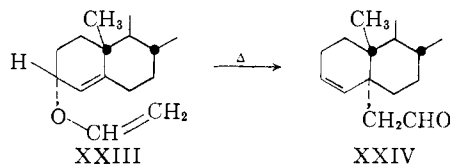

XXII

XXII
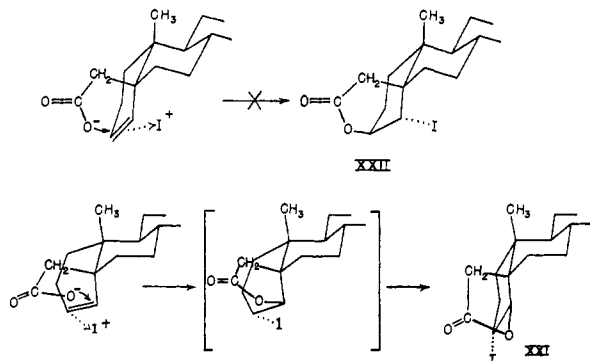
A possible explanation for this apparent anomaly can be seen from examination of molecular models, from which it is apparent that the otherwise fairly severe steric hindrance to the formation of an axial, α-side iodonium ion on ring A is relieved considerably if the attack occurs at C-3, with ring A in a quasi-boat conformation. Such behavior would lead, by *trans* coplanar addition, to the formation of a δ-iodo-γ-lactone (XXI), as observed.

Although rearrangement of the epimeric vinyl ether XXIII derived from Δ⁴-cholestene-3α-ol occurred readily enough, affording what is considered to be the unsaturated aldehyde XXIV, the formation of this quasi-axial vinyl ether by

the transetherification process[28] did not take place easily, and the yield was only about 5%. Since the success of this method for angular alkylation necessarily depends on the ease with which cyclic allylic alcohols of appropriate structure and configuration can be vinylated as well as prepared, this result with Δ⁴-cholestene-3α-ol, unless it can be improved considerably, indicates that possible future applications of the method might be severely limited. In any event, further work will be necessary before the full scope and usefulness of the process can be clearly defined.

Experimental[39]

dl-3-Allyloxymethylenecamphor (I).—A solution of 7.6 g. (0.042 mole) of *dl*-hydroxymethylenecamphor, m.p. 79–80°,[40] in 250 ml. (3.7 moles) of freshly dried and distilled allyl alcohol was treated with 10 drops of concd. sulfuric acid and then refluxed for 20 min.[41] Afterward, the mixture was cooled in an ice-bath and poured into 200 ml. of cold 5% sodium carbonate solution. Distillation of the product recovered by extraction of the mixture with ether furnished 8.7 g. (93% yield) of I, b.p. 97–98° (0.4 mm.), n^{20}D 1.5129.

Anal. Calcd. for $C_{14}H_{20}O_2$ (220.30): C, 76.32; H, 9.15. Found: C, 76.52; H, 8.91.

Pyrolysis of *dl*-3-Allyloxymethylenecamphor.—A 10-ml. sealed tube containing 5.6 g. (0.025 mole) of I under nitrogen was heated at 205 to 220° over a period of 40 min. The resulting product, which distilled at 74–75° (0.08 mm.), was dissolved in 10 ml. of petroleum ether, and the solution allowed to stand for several days at −20°. Large crystals of one of the isomers of *dl*-3-allyl-3-formylcamphor (II) slowly deposited. These weighed 2.6 g. (46% yield) and crystallized from the same solvent in elongated prisms, m.p. 51–53°, n^{20}D 1.4978 (supercooled sample), λmax 5.73 and 5.82 μ.

Anal. Calcd. for $C_{14}H_{20}O_2$ (220.30): C, 76.32; H, 9.15; O, 14.53. Found: C, 76.11; H, 8.99; O, 14.78.

(36) (a) M. Chuman, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **70**, 253 (1949) [*C. A.*, **45**, 6651 (1951)]; (b) J. H. Fried, G. E. Arth and L. H. Sarett, THIS JOURNAL, **82**, 1684 (1960); (c) J. H. Fried, A. N. Nutile and G. E. Arth, *ibid.*, **82**, 5704 (1960).

(37) *Cf.* D. H. R. Barton and R. C. Cookson, *Quart. Revs. (London)*, **10**, 44 (1956).

(38) *Cf.* G. H. Alt and D. H. R. Barton, *J. Chem. Soc.*, 4284 (1954); also D. H. R. Barton, D. A. Lewis and J. F. McGhie, *ibid.*, 2907 (1957).

(39) Melting points were taken on a microscope hot-stage calibrated against standard substances. Boiling points are uncorrected. Rotations (αD = specific rotation) were measured at 25–28° in chloroform at a concentration of 1 to 2%. Infrared spectra were determined in chloroform or, when specified, in carbon disulfide on a Perkin–Elmer model-137 Infracord or model-21 double beam spectrophotometer. Ultraviolet spectra were recorded in ethanol on a Beckman model DK·1 instrument. Petroleum ether refers to the fraction with b.p. 35–60°, unless indicated otherwise. Solid analytical samples were dried *in vacuo* at 80–100° or 30° below their melting points, whichever was lower. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(40) B. K. Singh and B. Bhaduri, *J. Indian Chem. Soc.*, **7**, 771 (1930).

(41) *Cf.* W. S. Johnson, J. W. Peterson and C. D. Gutsche, THIS JOURNAL, **69**, 2942 (1947).

The mono-2,4-dinitrophenylhydrazone of the preceding product crystallized from methanol–ethyl acetate in fine yellow prisms, m.p. 189–190°. The infrared spectrum (λ_{max} 5.73 μ; no band in the 5.8 μ region) indicated that only the aldehyde function had reacted.

Anal. Calcd. for $C_{20}H_{24}O_5N_4$ (400.42): C, 59.99; H, 6.04; N, 13.99. Found: C, 60.18; H, 6.10; N, 13.91.

Redistillation of the mother liquors from the crystallization of the above solid isomer of II furnished 2.2 g. (40% yield from I) of a fragrant liquid, b.p. 90–94° (0.15 mm.), $n^{20}D$ 1.5001. The mono-2,4-dinitrophenylhydrazone of this isomeric product crystallized from methanol–ethyl acetate in fine yellow needle clusters, m.p. 203–205°, λ_{max} 5.73 μ (no band in the 5.8 μ region).

Anal. Found: C, 60.10; H, 6.11; N, 13.82.

Preparation and Pyrolysis of Δ^2-Cyclohexenyl Acetoacetate (IIIa).—A solution of 3-bromo-Δ^1-cyclohexene[9] [from 82 g. (1.0 mole) of cyclohexene] in 350 ml. of tetrahydrofuran was added slowly to 2 moles of aqueous sodium bicarbonate and the mixture was stirred at 25° for 20 hr. After dilution with water, the mixture was extracted several times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate, the solvent evaporated, and the residue distilled under reduced pressure to give 44 g. of Δ^2-cyclohexenol, b.p. 50–55° (3.0 mm.), $n^{20}D$ 1.4879 (45% overall yield from cyclohexene).

To a solution of 23 g. (0.23 mole) of Δ^2-cyclohexenol and 4 ml. of pyridine in 150 ml. of sodium-dried ether at 0°, 19.1 g. (10% molar excess) of freshly distilled diketene (Aldrich Chemical Co., Milwaukee 12, Wisc.) was added, with stirring. After 4 hr. the temperature of the mixture was allowed to reach 25°. The mixture was then extracted with two 25-ml. portions of cold 3 N hydrochloric acid and once with 50 ml. of 10% aqueous sodium bicarbonate. The ether layer was dried and distilled, and the acetoacetic ester IIIa was collected at 77–79° (0.05 mm.), $n^{20}D$ 1.4791; yield 23.5 g. (55%). When 10 g. (0.055 mole) of this product was heated for 2 hr. at 170–180° (bath temp.), 1250 ml. of carbon dioxide (measured at 23° and 740 mm., 91% of theory) was evolved. Distillation (at 740 mm.) gave 2.3 g. of a fraction boiling at 56–60° (identified as acetone by the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 125–126°) and 1.5 g. of a second one boiling at 65–77° (identified as 1,3-cyclohexadiene by the maleic anhydride adduct,[42] m.p. 145–146°). The residue was refluxed for 1.5 hr. with 25 ml. of a sodium hydroxide in water and dioxane adjusted to single phase. Recovery of the neutral product by dilution of the hydrolysis mixture and extraction with ether afforded *ca.* 0.5 ml. of ketonic material distilling mostly over the range 170–190°; λ_{max} 5.85 μ. This gave 0.45 g. of the semicarbazone of Δ^2-cyclohexenylacetone (IVa) as fine plates from ethanol, m.p. 170–171°.

Anal. Calcd. for $C_{10}H_{17}ON_3$ (195.26): C, 61.51; H, 8.78; N, 21.52. Found: C, 61.72; H, 8.69; N, 21.28.

Catalytic hydrogenation of the preceding derivative over 10% palladium-on-charcoal in alcohol resulted in the absorption of one molar equivalent of hydrogen and furnished the semicarbazone of cyclohexylacetone, m.p. 173–174° (lit.[14] m.p. 165–166°; 182.5°). In another experiment, hydrogenation of the distilled ketone IVa afforded a product which gave this same derivative.

Preparation and Pyrolysis of 3-Methyl-Δ^2-cyclohexenyl Acetoacetate (IIIb).—A solution of 15 g. (0.136 mole) of 3-methyl-Δ^2-cyclohexenone[11] in 30 ml. of dry ether was added slowly, with stirring, to a solution (filtered) of 1.5 g. of lithium borohydride in ether cooled to −20°. The mixture was allowed to stand overnight at 0° and then for 4 hr. at 20°. After hydrolysis by the dropwise addition of water, the reaction mixture was stirred vigorously for 1 hr. at 25° with 100 ml. of water. The ether layer was separated, washed with two 30-ml. portions of water, and dried over anhydrous potassium carbonate. Filtration and evaporation of the solvent afforded an oily residue which on distillation gave 12 g. (79% yield) of 3-methyl-Δ^2-cyclohexenol, b.p. 70–71° (12 mm.), $n^{20}D$ 1.4854 [lit.[10] b.p. 56° (1 mm.), $n^{20}D$ 1.4822]. The α-naphthylurethane melted at 113–115° (lit.[10] 118–119°). Reduction of 0.2555 g. (2.28 mmoles) of the free alcohol over 10% palladium-on-charcoal in ethanol at 23° and 745 mm. required 52.0 ml. of hydrogen, corresponding to 92% of unsaturation. The infrared spectrum showed that no ketonic material was present. Alternatively,

reduction of 3-methyl-Δ^2-cyclohexenone with sodium borohydride in methanol at 0° furnished a product which gave an unsaturation assay of 100% by hydrogenation and was devoid of carbonyl absorption in the infrared.

From 15 g. (0.134 mole) of 3-methyl-Δ^2-cyclohexenol and 13.9 g. of diketene there was obtained, by the procedure described for the preparation of IIIa, 21.7 g. (83% yield) of the acetoacetic ester IIIb, b.p. 84–86° (0.2 mm.), $n^{20}D$ 1.4734.

Anal. Calcd. for $C_{11}H_{16}O_3$ (196.25): C, 67.32; H, 8.22. Found: C, 67.20; H, 8.46.

Catalytic reduction of 0.4160 g. (2.12 mmoles) of this ester resulted in the absorption of 51.9 ml. of hydrogen at 24° and 731 mm., corresponding to 2.05 mmoles, or 97% of unsaturation.

For pyrolysis, 15 g. of the ester was heated at 170–180° over a period of 1.5 hr. Besides carbon dioxide (90% of theory), a considerable amount of acetone and dienic material was liberated. The latter was washed with water, dried over magnesium sulfate and redistilled. The major fraction (2.5 g.) was collected at 106–107° (745 mm.) and showed λ_{max} 258 mμ (ϵ *ca.* 4,000) and 230 mμ (ϵ *ca.* 11,000). Gas chromatographic analysis on a silicone oil–fire-brick column indicated that the diene was probably a mixture of 3-methylenecyclohexene and 1- and 2-methyl-1,3-cyclohexadiene. Efforts to obtain a crystalline maleic anhydride adduct were unsuccessful.

Alkaline hydrolysis of the oily residue from the pyrolysis furnished *ca.* 3.5 g. of a fragrant ketonic product which, on distillation, gave three fractions ranging in boiling point from 80 to 120° (25 mm.), with the major portion (*ca.* 2.0 g.) distilling at 90–100°. The semicarbazones of these fractions crystallized readily from methanol in fine plates, m.p. 145–160°. On hydrogenation each showed exactly one molar equivalent of double bond, based on structure IVb or IVc. The resulting dihydro semicarbazones melted at 137–138° after several recrystallizations from methanol and did not depress each other on admixture. A crystalline 2,4-dinitrophenylhydrazone could not be obtained. Gas chromatography of the regenerated ketone (from the middle-cut semicarbazone) on a 2.5-meter polypropylene glycol-Celite column at 160° gave two major peaks with retention times of 8.6 and 9.2 min. (helium carrier at 25 p.s.i.). Comparison of the relative peak heights and positions with those of authentic samples (see below) of 1-methyl- and 3-methyl-cyclohexylacetone (dihydro IVb and IVc, respectively), showed that the ketone consisted of approximately three parts of the former and one part of the latter.

Authentic 1-Methylcyclohexylacetone.—To a solution of dimethylcadmium in benzene–ether at 0° (prepared from 0.05 mole of methylmagnesium iodide and 5.8 g. of anhydrous cadmium chloride), 7.0 g. of 1-methylcyclohexylacetyl chloride, obtained as described below in the preparation of authentic 1-methylcyclohexylacetaldehyde, was added, with stirring. The temperature of the reaction was allowed to rise to 25°, and stirring was continued for 12 hr. Hydrolysis of the mixture and distillation of the neutral product afforded 3.5 g. (56% yield) of a highly fragrant liquid, characterized by the derivatives below as 1-methylcyclohexylacetone, b.p. 92–95° (18 mm.), $n^{20}D$ 1.4584, λ_{max} 5.85 μ. The retention time of this product on gas chromatography under the conditions used for the separation of the dihydro IVb–IVc mixture was 8.8 min.

The semicarbazone of 1-methylcyclohexylacetone crystallized from dilute ethanol in fine plates, m.p. 186–187°.

Anal. Calcd. for $C_{11}H_{21}ON_3$ (211.30): C, 62.52; H, 10.02; N, 19.89. Found: C, 62.76; H, 9.98; N, 19.66.

The 2,4-dinitrophenylhydrazone deposited slowly from ethanol in large orange rhombic crystals, m.p. 84–85.°

Anal. Calcd. for $C_{16}H_{22}O_4N_4$ (334.37): C, 57.47; H, 6.63; N, 16.76. Found: C, 57.67; H, 6.80; N, 16.93.

Authentic 3-Methylcyclohexylacetone.—By means of the Reformatsky procedure 31 g. (0.276 mole) of 3-methyl-cyclohexanone (prepared by catalytic hydrogenation of 3-methyl-Δ^2-cyclohexenone over palladium-on-charcoal) afforded, on reaction with ethyl bromoacetate, 34 g. of the corresponding hydroxy ester, b.p. 80–85° (1.2 mm.).[16] Dehydration of this product by the action of phosphorus oxychloride in pyridine at 0° and then at 25° provided an unsaturated ester, which was hydrogenated directly over platinum oxide. Hydrolysis of the resulting product furnished 13.3 g. of 3-methylcyclohexylacetic acid, b.p. 84–89°

(42) O. Diels and K. Alder, *Ann.*, 460, 98 (1928).

(0.5 mm.). This acid, with thionyl chloride, gave 13.9 g. of the corresponding acid chloride, b.p. 102–103° (18 mm.), n^{20}D 1.4753. By reaction with dimethylcadmium as described above, 13.5 g. (0.077 mole) of this acid chloride furnished 7.1 g. (60% yield) of 3-methylcyclohexylacetone, b.p. 95–98° (18 mm.), n^{20}D 1.4600, λ_{max} 5.85 μ. The retention time of this product on gas chromatography under the conditions indicated earlier was 9.2 min.

The semicarbazone of 3-methylcyclohexylacetone crystallized from dilute ethanol in irregular plates, m.p. 154–156° (lit.[16] 154°).

Anal. Calcd. for $C_{11}H_{21}ON_3$ (211.30): C, 62.52; H, 10.02; N, 19.89. Found: C, 62.75; H, 9.85; N, 19.96.

The 2,4-dinitrophenylhydrazone deposited from ethanol in irregular yellow plates, m.p. 91–94°.

Anal. Calcd. for $C_{16}H_{22}O_4N_4$ (334.37): C, 57.42; H, 6.63; N, 16.76. Found: C, 57.41; H, 6.48; N, 16.49.

Preparation and Rearrangement of Δ^2-Cyclohexenyl Vinyl Ether (Va).—For satisfactory results in the vinyl trans-etherification reaction[23] it was necessary to employ mercuric acetate that had been carefully recrystallized from absolute ethanol and thoroughly dried. The ethyl vinyl ether (U.S. Carbide and Carbon) was washed free of stabilizer with cold 2 N hydrochloric acid and then extracted with 2 N sodium hydroxide. After being dried over anhydrous potassium carbonate it was distilled over sodium wire and stored in the dark at 0° until use.

Vinylations were conducted according to the method B of Watanabe and Conlon,[23] with slight modifications. In the present instance a solution containing 20 g. (0.202 mole) of Δ^2-cyclohexenol and 145 g. (2 moles) of ethyl vinyl ether was treated at reflux with 3.0 g. of mercuric acetate over a period of 3 hr. and then allowed to reflux for an additional 6 hr. The mixture was cooled in an ice-bath and stirred for 30 min. with 100 ml. of cold 10% sodium carbonate solution. The upper layer was separated, dried briefly over anhydrous potassium carbonate, and finally fractionated through a 4-inch Vigreux column under reduced pressure. Material boiling at 45–52° (10–12 mm.) was collected and redistilled rapidly from sodium to give Δ^2-cyclohexenyl vinyl ether (Va), b.p. 48–48.5° (10 mm.), n^{20}D 1.4740, yield 8.9 g. (35%). The infrared spectrum displayed typical strong vinyl ether absorption at 6.1, 6.2 and 8.4 μ.

Anal. Calcd. for $C_8H_{12}O$ (124.18): C, 77.37; H, 9.74. Found: C, 77.31; H, 9.95.

For rearrangement, in a typical experiment, a 5.25-gram sample (0.0422 mole) of the above product was heated for 15 min. at 190–195° under nitrogen in a fully immersed, half-filled, sealed tube. Direct distillation gave 4.91 g. (94% yield) of a colorless, sharp-smelling product, b.p. 65–66° (11 mm.), n^{20}D 1.4746, λ_{max} 3.7(w) and 5.8(s) μ. This was characterized as Δ^2-cyclohexenylacetaldehyde as follows.

The 2,4-dinitrophenylhydrazone crystallized in practically quantitative yield from ethanol–ethyl acetate in light orange, flattened needles, m.p. 93–94°.

Anal. Calcd. for $C_{14}H_{16}O_4N_4$ (304.30): C, 55.25; H, 5.30; N, 18.41. Found: C, 55.49; H, 5.50; N, 18.49.

The semicarbazone crystallized from dilute methanol in plates, m.p. 144–145.5°.

Anal. Calcd. for $C_9H_{15}ON_3$ (181.23): C, 59.64; H, 8.34; N, 23.19. Found: C, 59.79; H, 8.20; N, 22.97.

Hydrogenation of 0.3077 g. (1.695 mmoles) of the foregoing semicarbazone in ethanol with 10% palladium-on-carbon resulted in the absorption of 44.0 ml. of hydrogen at 23° and 745 mm. (theory 42.5 ml.). Separation of the catalyst and evaporation of the solvent afforded the semicarbazone of cyclohexylacetaldehyde, which crystallized from dilute methanol as rectangular plates, m.p. 161–162.5°. Various recorded values for the melting point of this substance are 132–134°,[24] 153°,[43] 158–159°,[44] 162°,[45] and 171–172°.[46]

The 2,4-dinitrophenylhydrazone, as obtained from the preceding semicarbazone, crystallized from methanol–ethyl

acetate in glistening orange plates, m.p. 123–124.5° (lit.[44] 124–125°).[47]

Anal. Calcd. for $C_{14}H_{18}O_4N_4$ (306.32): C, 54.89; H, 5.92; N, 18.29. Found: C, 55.07; H, 6.27; N, 17.96.

For further characterization, 3.5 g. (0.0281 mole) of the rearrangement product VIa was oxidized to the corresponding acid by the action of silver oxide (prepared from 12 g. of silver nitrate) in ethanol–water at 45–50° and pH 10. After 12 hr. the mixture was filtered, the neutral material removed by extraction with ether, and the aqueous layer acidified with cold 6 N sulfuric acid. The Δ^2-cyclohexenylacetic acid (VIIa) recovered by extraction with ether and distillation weighed 3.4 g. (86% yield) and had b.p. 91–93° (0.05 mm.), n^{20}D 1.4805. By the procedure of van Tamelen and Shamma[26] a portion of this product was converted to the corresponding δ-iodo-γ-lactone VIIIa, which crystallized from ethanol–petroleum ether as stubby needles, m.p. 65–66°, λ_{max} 5.61 μ (lit.[26] m.p. 65–66°, λ_{max} 5.62 μ).

Preparation and Rearrangement of 3-Methyl-Δ^2-cyclohexenyl Vinyl Ether (Vb).—Application of the above-modified Watanabe–Conlon vinylation procedure[23] to 11.0 g. (0.098 mole) 3-methyl-Δ^2-cyclohexenol furnished 5.6 g. (41% yield) of redistilled 3-methyl-Δ^2-cyclohexenyl vinyl ether (Vb), b.p. 59–60° (12 mm.), n^{20}D 1.4702; λ_{max} 6.1, 6.2 and 8.4 μ.

Anal. Calcd. for $C_9H_{14}O$ (138.20): C, 78.21; H, 10.21. Found: C, 78.53; H, 10.50.

On catalytic reduction 0.1957 g. (1.41 mmoles) of this product absorbed 68.0 ml. of hydrogen at 23° and 745 mm. (97% of theory for two double bonds).

Rearrangement of 5.60 g. (0.0405 mole) of the above vinyl ether at 195–200° for 15 min. gave, after distillation, 5.19 g. (93% yield) of 1-methyl-Δ^2-cyclohexenylacetaldehyde (VIb), b.p. 73–75° (10 mm.), n^{20}D 1.4713, λ_{max} 3.7(w) and 5.8(s) μ. The 2,4-dinitrophenylhydrazone, which crystallized from ethanol–ethyl acetate as deep yellow plates, m.p. 97–99°, was formed in 98.5% yield.

Anal. Calcd. for $C_{15}H_{18}O_4N_4$ (318.33): C, 56.59; H, 5.70; N, 17.60. Found: C, 56.40; H, 5.73; N, 17.46.

The semicarbazone of VIb crystallized from ethanol as needles, m.p. 171–172°.

Anal. Calcd. for $C_{10}H_{17}ON_3$ (195.26): C, 61.51; H, 8.78; N, 21.52. Found: C, 61.51; H, 9.03; N, 21.25.

Catalytic hydrogenation of the free aldehyde VIb over palladium-on-charcoal furnished a product whose 2,4-dinitrophenylhydrazone crystallized from ethanol in large, dimorphic prisms having a double m.p. 85–87° and 103–106° (lit.[25] 84–85°).

Anal. Calcd. for $C_{15}H_{20}O_4N_4$ (320.34): C, 56.24; H, 6.29; N, 17.49. Found: C, 55.94; H, 6.52; N, 17.41.

The semicarbazone of the reduction product crystallized from dilute ethanol as plates, m.p. 181–182° (lit.[25] 177–178°).

Anal. Calcd. for $C_{10}H_{19}ON_3$ (197.28): C, 60.88; H, 9.71; N, 21.30. Found: C, 61.17; H, 9.71; N, 21.47.

The melting points of mixtures of the above derivatives with authentic samples prepared as described below showed no depression.

1-Methyl-Δ^2-cyclohexenylacetic Acid (VIIb).—From the oxidation of 3.0 g. (0.022 mole) of VIb with silver oxide, as described for the conversion of VIa to VIIa, there was obtained 2.3 g. (68% yield) of 1-methyl-Δ^2-cyclohexenylacetic acid (VIIb), b.p. 93–95° (0.05 mm.), n^{20}D 1.4810.

Anal. Calcd. for $C_9H_{14}O_2$ (154.20): C, 70.10; H, 9.15. Found: C, 70.10; H, 8.90.

The corresponding δ-iodo-γ-lactone VIIIb crystallized from absolute ethanol–petroleum ether as jagged prisms, m.p. 79–81°, λ_{max} 5.61 μ.

Anal. Calcd. for $C_9H_{13}O_2I$ (280.12): C, 38.59; H, 4.68; I, 45.31. Found: C, 38.66; H, 4.42; I, 45.20.

Authentic 1-Methylcyclohexylacetaldehyde.—The Diels-Alder adduct of butadiene and methyl methacrylate (100 g., 1.0 mole) was prepared according to the directions of

(43) A. Skita, *Ber.*, **48**, 1685 (1915).

(44) J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 566 (1941).

(45) F. Sigmund, *Monatsh.*, **49**, 271 (1928).

(46) H. Rupe, W. Messner and E. Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

(47) This m.p. is mistakenly attributed to the authors of ref. 46 by C. M. Hill, H. E. Hill, H. I. Schofield and L. Haynes, THIS JOURNAL, **74**, 166 (1952), who, interestingly, report a m.p. of 64–65° for this derivative. In this connection it should be noted that the physical constants of a number of the ω-cyclohexyl-substituted aliphatic aldehydes recorded by Hill, *et al.*, are obviously listed incorrectly.

Petrov and Sopov.[48] The b.p. of the product was 79–83° (18 mm.), n^{20}D 1.4602, yield 60 g. (39%). Catalytic hydrogenation of this material over palladium-on-charcoal furnished the corresponding saturated ester, which was not isolated, but was hydrolyzed directly with 3 N sodium hydroxide in ethylene glycol at 120°, giving, after acidification of the mixture, extraction with ether, and distillation, 1-methylcyclohexanecarboxylic acid, b.p. 78–81° (1 mm.) [lit.[49] 137–138° (24 mm.)]. This substance set to a crystalline mass at room temperature (lit.[49] m.p. 38–39°). The corresponding acid chloride, b.p. 80–86° (22 mm.), was obtained in 80% yield by the action of thionyl chloride. Addition of 4.4 g. of the acid chloride to 0.1 mole of dry diazomethane in ether furnished, after 12 hr. at 0°, an oily diazoketone (λ_{max} 4.7 and 6.1 μ), which was treated with silver oxide in aqueous dioxane at 70°, thereby providing 2.3 g. (54% yield) of 1-methylcyclohexylacetic acid, b.p. 140–145° (20 mm.). Reaction of this acid with thionyl chloride afforded 1.6 g. of the corresponding acid chloride, b.p. 95–100° (15 mm.), n^{20}D 1.4792. Rosenmund reduction of the latter (in toluene) furnished 0.8 g. of 1-methylcyclohexylacetaldehyde,[25] b.p. 75–80° (10 mm.) [lit.[25] 78–80° (12 mm.)]. This product was converted in part to the semicarbazone, m.p. 181–182° (lit.[25] 177–178°), and in part to the 2,4-dinitrophenylhydrazone, double m.p. 84–86° and 103–106° (lit.[25] 84–85°).

By reaction with concd. ammonium hydroxide the above acid chloride of 1-methylcyclohexylacetic acid was converted to the corresponding acid amide, which, after recrystallization from dilute ethanol, melted at 113–114°.

Anal. Calcd. for $C_9H_{17}ON$ (155.23): C, 69.63; H, 11.04; N, 9.02. Found: C, 69.88; H, 11.07; N, 8.90.

$\Delta^{9(10)}$-1-Octalyl Vinyl Ether (IX).—1-Methoxy-5,6,7,8-tetrahydronaphthalene, b.p. 120–122° (25 mm.), n^{25}D 1.5446 [lit.[50] b.p. 85–88° (3 mm.), n^{25}D 1.5440] was prepared in 90–95% yield by catalytic hydrogenation of 1-methoxynaphthalene over W-5 Raney nickel[51] at 90–100° and a pressure of 1500 p.s.i. Its conversion, in 0.5-mole runs, to $\Delta^{9(10)}$-1-octalone was achieved essentially according to the method of Wilds and Nelson,[28] except that the free ketone was isolated by hydrolysis of the distilled reduction product in dilute ethanol with 1 N hydrochloric acid. The yield of octalone from the methoxytetralin, as determined by the 2,4-dinitrophenylhydrazone,[28] was 40–45%. For purification, the ketone was converted to the oxime, m.p. 147–148°,[52] and regenerated by digestion of the latter with alcoholic hydrochloric acid. Alternatively, the ketone could be purified through the Girard-T derivative. The infrared spectrum of the product from either method displayed an intense band at 6.0 μ (conjugated ketone) and a much weaker one at 5.85 μ (unconjugated or saturated ketone). The latter band was significantly weaker in the product from the Girard-T reagent. The redistilled ketone had b.p. 67–69° (0.1 mm.), n^{20}D 1.5241, λ_{max} 245 mμ (ϵ 14,000). Its purity, as assayed by hydrogenation or by the 2,4-dinitrophenylhydrazone, m.p. 267–268°,[28] was 98%.

Reduction of 15 g. (0.10 mole) of $\Delta^{9(10)}$-1-octalone with 1 g. of lithium borohydride in ether at 0° for 12 hr. furnished 11.5 g. (76% yield) of $\Delta^{9(10)}$-1-octalol, b.p. 72–74° (0.05 mm.), n^{20}D 1.5207. Catalytic hydrogenation of this product in ethanol over 10% palladium-on-carbon indicated the presence of unsaturation to the extent of about 92% of the theoretical. Vinylation[23] of 13.0 g. (0.085 mole) of the octalol provided, after rapid distillation from sodium at reduced pressure, 6.35 g. (41.5% yield) of $\Delta^{9(10)}$-1-octalyl vinyl ether (IX), b.p. 45–48° (0.09 mm.), n^{20}D 1.5005; λ_{max} 6.1, 6.2 and 8.5 μ.

Anal. Calcd. for $C_{12}H_{18}O$ (178.26): C, 80.85; H, 10.18. Found: C, 80.88; H, 10.38.

An alternative method for the purification of this vinyl ether involved rapid passage of the crude product over basic alumina (Woelm, activity grade 1) in low boiling petroleum ether (b.p. 38–42°), and then distillation of the material

at reduced pressure. Hydrogenation of various preparations of the vinyl ether indicated the presence of 1.8 to 1.9 moles of unsaturation per mole of ether.

$\Delta^{4(10)}$-9-Octalylacetaldehyde (X).—Rearrangement of 2.70 g. (0.015 mole) of the octalyl vinyl ether IX in a sealed tube at 195° for 1 hr. furnished 2.35 g. (87% yield) of $\Delta^{4(10)}$-9-octalylacetaldehyde (X) as a colorless fragrant oil, b.p. 62–63° (0.1 mm.), n^{20}D 1.5101, λ_{max} 3.7 and 5.81 μ.

Anal. Calcd. for $C_{12}H_{18}O$ (178.28): C, 80.85; H, 10.18. Found: C, 81.11; H, 10.26.

A small, low-boiling forerun (*ca.* 0.2 g.), having an intense λ_{max} at 243 mμ (ϵ *ca.* 12,000) suggestive of 2,3,4,6,7,-8-hexahydronaphthalene (XI),[53] was noted in the distillation of the foregoing product.

The semicarbazone of X crystallized from dimethylformamide–methanol in flattened prisms, m.p. 204–206°.

Anal. Calcd. for $C_{13}H_{21}ON_3$ (235.32): C, 66.35; H, 9.00; N, 17.86. Found: C, 66.10; H, 8.80; N, 17.80.

Assay of the distilled aldehyde by means of this derivative indicated the purity of X to be *ca.* 75–80%, which is in agreement with the already noted hydrogenation assay of the vinyl ether IX.

The 2,4-dinitrophenylhydrazone of X deposited from ethanol–ethyl acetate as orange plates, m.p. 118–121°.

Anal. Calcd. for $C_{18}H_{22}O_4N_4$ (358.39): C, 60.32; H, 6.19; N, 15.63. Found: C, 60.08; H, 6.43; N, 15.59.

cis-9-Decalylacetaldehyde.—Hydrogenation of 2.7 g. (0.015 mole) of X in ethanol over 10% palladium-on-carbon required 2 hr. at a temperature of 25° and a pressure of one atmosphere and resulted in the absorption of 355 ml. of hydrogen (96% of theory). The product was a fragrant oil which was characterized without formal purification. The 2,4-dinitrophenylhydrazone crystallized from ethanol–ethyl acetate in light orange plates, m.p. 126.5–127.5°.

Anal. Calcd. for $C_{18}H_{24}O_4N_4$ (360.40): C, 59.98; H, 6.71; N, 15.55. Found: C, 60.19; H, 6.85; N, 15.53.

The semicarbazone crystallized from dimethylformamide as needles, m.p. 203–204°.

Anal. Calcd. for $C_{13}H_{23}ON_3$ (273.34): C, 65.78; H, 9.77; N, 17.71. Found: C, 65.74; H, 9.87; N, 17.85.

Treatment of 2.0 g. of the reduction product with silver oxide in ethanol for 12 hr. at 60° with stirring resulted in the formation of 0.45 g. of acidic product which crystallized from dilute ethanol as fine needles, m.p. 114–115°, in agreement with the recorded[30] m.p. of *cis*-9-decalylacetic acid. The anilide, prepared by the thionyl chloride–aniline technique, crystallized from dilute ethanol in slender needles, m.p. 154–156°, also in agreement with the recorded[30] m.p. Barbier–Wieland degradation of the acid according to the directions of Haworth and Turner[30] afforded *cis*-9-decalincarboxylic acid, m.p. 120–122° (lit.[30,31] 122°). A mixed melting point with an authentic sample of *cis*-9-decalincarboxylic acid kindly supplied by Professor William G. Dauben[31] was undepressed.

$\Delta^{4(10)}$-9-Octalylacetic Acid (XII).—Oxidation of 1.8 g. of the distilled rearrangement product X with silver oxide (prepared from 5 g. of silver nitrate) in dilute ethanol at pH 9–10 and 60° for 20 hr. resulted in the formation of 0.55 g. of an acidic product (XII), which crystallized from benzene–petroleum ether in elongated prisms, m.p. 103–106° (soft. 95°).

Anal. Calcd. for $C_{12}H_{18}O_2$ (194.26): C, 74.19; H, 9.34. Found: C, 73.76; H, 9.28.

Catalytic hydrogenation of XII furnished a mixture containing predominantly *cis*-9-decalylacetic acid.

The corresponding iodolactone (XIV), obtained in the usual manner,[28] crystallized from ethanol–ethyl acetate as coarse prism clusters, m.p. 165–167.5°, λ_{max} 5.65 μ.

Anal. Calcd. for $C_{12}H_{18}O_2I$ (321.17): C, 44.87; H, 5.65; I, 39.52. Found: C, 45.05; H, 5.61; I, 39.46.

cis- and *trans*-9-Ethyldecalin. A.—An intimate mixture of 2.8 g. of the semicarbazone (m.p. 208–210°) of the octalylacetaldehyde X and 4.2 g. of pulverized potassium hydroxide was placed in a 25-ml. distillation flask and heated strongly in a Wood's metal-bath. At 235° (bath temp.) the mixture became molten, and at 290° a fragrant, mobile oil began to distil. After completion of the distillation

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(bath temp. 300°) the crude 9-ethyl-$\Delta^{4(10)}$-octalin (XIII) was dried briefly over anhydrous sodium sulfate and the refractive index determined: n^{20}D 1.5021. Hydrogenation of this material in ethanol over 10% palladium-on-charcoal required 2 hr. After filtration, the solution was diluted with water and extracted with three 5-ml. portions of ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated. Distillation of the residue from sodium gave 1.01 g. of a pleasant-smelling hydrocarbon, b.p. ca. 210° (740 mm.), n^{20}D 1.4869. On the basis of gas chromatography on a 6-foot silicone–firebrick column at 160°, this product appeared to be a mixture consisting of ca. 3 parts of cis- to 4 parts of trans-9-ethyldecalin (retention times 43.8 and 40.5 min., respectively, as compared to the major peak at 44.2 min. for the predominantly cis-9-ethyldecalin prepared as described below in part B).

Anal. Calcd. for $C_{12}H_{22}$ (166.30): C, 86.66; H, 13.34. Found: C, 86.53; H, 13.48.

B.—A 1.3-g. sample of the once-recrystallized semicarbazone (m.p. 198–205°) of the 9-decalylacetaldehyde obtained by hydrogenation of the octalylacetaldehyde X was mixed with 2 g. of powdered potassium hydroxide and the mixture heated to 225° and then slowly to 300° (bath temp.). After having been dried in ether over anhydrous magnesium sulfate, the resulting 9-ethyldecalin was redistilled from sodium; b.p. ca. 210°, n^{20}D 1.4877, yield 0.67 g. Relative peak areas in the gas chromatogram obtained under conditions described in part A indicated a 5:2 cis to trans isomer ratio (retention times 44.2 and 40.7 min., respectively).

Anal. Found: C, 86.42; H, 13.25.

Δ^4-3β-Cholestenyl Vinyl Ether (XV).—A cold (0°) solution of 15 g. (0.039 mole) of Δ^4-cholestene-3-one,[54] m.p. 79–80°, in 200 ml. of ether-benzene (8:1) was added dropwise to 0.05 mole of lithium tri-t-butoxyaluminum hydride in ether-diglyme[55] at −40° to −50°. The mixture was allowed to stand overnight at 0° and was then hydrolyzed by treatment with ice, 5 N sodium hydroxide and Rochelle salts. Evaporation of the washed and dried ether extracts and crystallization of the residue from ethyl acetate afforded 13 g. (87% yield) of nearly pure Δ^4-cholestene-3β-ol, m.p. 126–129°. One recrystallization from the same solvent gave the pure product in large needles, m.p. 131–132°, αD +46° (lit.[56] m.p. 132°, αD +44° benzene).

In a typical experiment, for conversion to the vinyl ether XV, 4.7 g. (12.1 mmoles) of the above material and 1.5 g. of freshly recrystallized mercuric acetate were dissolved in 100 ml. of purified ethyl vinyl ether, and the solution was refluxed for 10 hr., with an additional 0.5 g. of mercuric acetate being added every 2 hr. After extraction with cold aqueous sodium carbonate, the solution was dried, concentrated, and the residue chromatographed rapidly on 90 g. of basic alumina (Woelm, activity grade 1). The fraction eluted with 500 ml. of petoleum ether (b.p. 38–42°) gave 3.0 g. (65% yield) of 3β-vinyloxy-Δ^4-cholestene (XV) which recrystallized at 0° from chloroform–ethanol in large needle clusters, m.p. 56–57°, αD +10.5°; λ_{max} 6.1, 6.2 and 8.4 μ.

Anal. Calcd. for $C_{29}H_{48}O$ (412.67): C, 84.40; H, 11.72. Found: C, 84.61; H, 11.90.

Δ^3-5β-Cholestenylacetaldehyde (XVI).—In a representative experiment, a solution of 0.676 g. (1.64 mmoles) of XV in 4.5 ml. of redistilled decalin was heated under nitrogen in a sealed tube at 195° for 4 hr. (rearrangement incomplete after 2 hr.). Evaporation of the decalin on the steam-bath at reduced pressure left a colorless oil which crystallized from ethanol at 0° to furnish 0.561 g. (83% yield) of Δ^3-5β-cholestenylacetaldehyde (XVI) in fine plates, m.p. 66–69°, αD +85°; $\lambda_{max}^{CS_2}$ 3.7(w), 5.8(s), 13.6(w) and 14.5(w)μ.

Anal. Calcd. for $C_{29}H_{48}O$ (412.67): C, 84.40; H, 11.72. Found: C, 84.55; H, 11.71.

Rearrangement of the vinyl ether XV in carefully dried diglyme redistilled from sodium was about equally satis-

factory. Interestingly, chromatography of the rearrangement product on alumina (Woelm, non-alkaline, activity grade 1) resulted in extensive by-product formation (conjugated carbonyl band in the infrared spectrum).

The n.m.r. spectrum[34] showed methylene spin–spin coupling (8 bands), consistent with the attachment of a formyl-methyl group to a quaternary carbon atom, and also contained an olefinic proton absorption pattern characteristic of a Δ^3-steroid.

The oxime of XVI crystallized from methanol–ethyl acetate in small needles, m.p. 133–136°, αD +111°.

Anal. Calcd. for $C_{29}H_{49}ON$ (427.69): C, 81.44; H, 11.55; N, 3.28. Found: C, 81.72; H, 11.41; N, 3.15.

The 2,4-dinitrophenylhydrazone of XVI deposited from ethanol–ethyl acetate in fine yellow plates, m.p. 167–169°.

Anal. Calcd. for $C_{35}H_{52}O_4N_4$ (592.80): C, 70.90; H, 8.84; N, 9.45. Found: C, 71.11; H, 9.01; N, 9.55.

The semicarbazone of XVI, recrystallized from dimethylformamide, formed micro-needles, m.p. 230–232°.

Anal. Calcd. for $C_{30}H_{51}ON_3$ (469.74): C, 76.70; H, 10.94; N, 8.95. Found: C, 76.84; H, 10.98; N, 8.66.

5β-Cholestanylacetaldehyde (XVIII).—Hydrogenation of 0.271 g. (0.66 mmole) of XVI with 10% palladium-on-charcoal in ethanol resulted in the absorption of 16.0 ml. of hydrogen at 24° and 745 mm. (theory 16.4 ml.). Purification of the product by passage over 5 g. of neutral alumina (Woelm, non-alkaline, activity grade 1) with benzene–chloroform (1:1) and crystallization from ethanol-ethyl acetate (Dry Ice-bath) furnished 0.21 g. of 5β-cholestanylacetaldehyde (XVIII) as fine prism clusters, m.p. 58–61°, αD +42°, λ_{max} 3.7(w) and 5.81(s) μ.

Anal. Calcd. for $C_{29}H_{50}O$ (414.69): C, 83.99; H, 12.15. Found: C, 84.10; H, 12.16.

Crystallized from dilute ethanol, the oxime of XVIII formed in small needles, m.p. 64–65°, αD +59°.

Anal. Calcd. for $C_{29}H_{51}ON$ (429.71): C, 81.05; H, 11.96; N, 3.26. Found: C, 81.21; H, 11.81; N, 3.29.

The 2,4-dinitrophenylhydrazone of XVIII crystallized from ethanol–ethyl acetate in small yellow plates, m.p. 163–165° (sint. 158°).

Anal. Calcd. for $C_{35}H_{54}O_4N_4$ (594.81): C, 70.67; H, 9.15; N, 9.42. Found: C, 70.60; H, 9.19; N, 9.14.

The semicarbazone of XVIII deposited from dimethylformamide in fine plates, m.p. 236–237°.

Anal. Calcd. for $C_{30}H_{53}ON_3$ (471.75): C, 76.38; H, 11.32; N, 8.91. Found: C, 76.54; H, 11.24; N, 8.67.

5β-Cholestanylacetic Acid (XIX).—Oxidation of XVIII by the action of silver oxide in dilute ethanol at 60° furnished, in about 35% yield, 5β-cholestanylacetic acid (XIX), which crystallized from ethanol–benzene or ethanol–ethyl acetate in short, fine needles, m.p. 222–224° (cap.) or 213–216° (H.S.), αD +72°.

Anal. Calcd. for $C_{29}H_{50}O_2$ (430.69): C, 80.87; H, 11.70. Found: C, 80.88; H, 11.73.

The methyl ester (diazomethane) of XIX crystallized from methanol–ethyl acetate as small plates, m.p. 111–112°, αD +75°.

Anal. Calcd. for $C_{30}H_{52}O_2$ (444.72): C, 81.02; H, 11.79. Found: C, 80.96; H, 11.97.

5β-Ethylcholestane (XX).—Treatment of 0.331 g. (0.8 mmole) of the cholestanylacetaldehyde XVIII with 0.5 ml. of ethanedithiol and 0.5 ml. of boron trifluoride etherate in 0.5 ml. of benzene at 70° for 20 min.[57] furnished, after dilution with ether, extraction with 1 N sodium hydroxide and evaporation of the solvent, a colorless oil devoid of carbonyl absorption in the infrared. This oil was then dissolved in 40 ml. of ethanol, 10 g. of Raney nickel was added, and the mixture heated at reflux for 10 hr. Filtration, evaporation of the solvent, and passage of the residue over 10 g. of alumina (Woelm, non-alkaline, activity grade 1) with 100 ml. of petroleum ether afforded a colorless oil, which, on crystallization from methanol–ethyl acetate, deposited 0.172 g. (54% yield) of 5β-ethylcholestane (XX) as irregular plates, m.p. 67–69°, αD +18°.

Anal. Calcd. for $C_{29}H_{52}$ (400.71): C, 86.92; H, 13.08. Found: C, 87.17; H, 12.87.

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Δ^3-5β-Cholestenylacetic Acid (XVII) and the Iodolactone XXI.—Silver oxide oxidation of the cholestenylacetaldehyde XVI provided, in 40% yield, the corresponding acid (XVII), which crystallized from ethanol–ethyl acetate in fine, short needles, m.p. 217–219° (cap.) and 209–212° (H.S.), αD +97°.

Anal. Calcd. for $C_{29}H_{48}O_2$ (428.67): C, 81.25; H, 11.29. Found: C, 81.38; H, 11.51.

The methyl ester of XVII (diazomethane) deposited from methanol–ethyl acetate in plates, m.p. 116–118°, αD +98°.

Anal. Calcd. for $C_{30}H_{50}O_2$ (442.70): C, 81.39; H, 11.38. Found: C, 81.44, H, 11.54.

Catalytic hydrogenation of this derivative in ethanol over platinum oxide furnished the methyl ester of XIX, m.p. and mixed m.p. 111–112°.

Application of the iodolactonization reaction[26,27] to the sodium salt of XVII in dilute solution afforded, in 60% yield, the corresponding δ-iodo-γ-lactone (XXI), which crystallized from methanol–ethyl acetate in short needles, m.p. 230–231°, αD +35°, λ_{max} 5.65 μ.

Anal. Calcd. for $C_{29}H_{47}O_2I$ (554.61): C, 62.80; H, 8.54; I, 22.91. Found: C, 62.70; H, 8.61; I, 23.06.

Δ^3-5α-Cholestenylacetaldehyde (XXIV).—Vinylation of 800 mg. of Δ^4-cholestene-3α-ol,[56] m.p. 81–84°, αD +119° (lit.[56] m.p. 84°, αD +121° benzene) furnished, by the procedure used for the preparation of XV, *ca.* 60 mg. of oily chromatographed vinyl ether XXIII, λ_{max} 6.1, 6.2 and 8.4 μ, which appeared to contain some conjugated impurity (λ_{max} 265–270 mμ). Rearrangement of the crude ether in decalin at 190–195° for 3 hr. afforded an aldehydic product (λ_{max} 5.81 μ), from which a crystalline semicarbazone was prepared. Recrystallized from benzene-ethanol, this derivative weighed 13 mg. and melted at 227–229° (depressed to 222–226° on admixture with the semicarbazone, m.p. 230–232°, of XVI).

Anal. Calcd. for $C_{30}H_{51}ON_3$ (469.74): C, 76.70; H, 10.94; N, 8.95. Found: C, 76.94; H, 11.09; N, 8.69.

Cycloheptatrienes from the Solvolysis of 1,4-Dihydrobenzyl p-Toluenesulfonates[1]

BY NORMAN A. NELSON,[2] JOHN H. FASSNACHT[3] AND JAMES U. PIPER

The conversion of aromatic carboxylic acids to 1,4-dihydrobenzyl p-toluenesulfonates is described. Solvolysis of the p-toluenesulfonates in acetic acid containing sodium dihydrogen phosphate gives chiefly cycloheptatrienes with lesser amounts of esters and aromatic hydrocarbons. The preparations of cycloheptatriene, 1-, 2- and 3-methylcycloheptatriene and 1,2-benzo-3-methylcycloheptatriene are described.

The unusual properties and uses of cycloheptatrienes has led to a variety of methods for the preparation of the parent compound.[4] While some of these methods are capable of being extended to the preparation of substituted cycloheptatrienes, little work has been done in this direction. In a preliminary communication,[5] we reported briefly a synthesis of cycloheptatriene and three of the four possible methylcycloheptatrienes. This paper discloses the details of this new method for preparing cycloheptatrienes.

The availability of 1,4-dihydrobenzoic acids by metal–ammonia reduction of the aromatic acids[6] and of 1-alkyl-1,4-dihydrobenzoic acids by alkylation of the 1,4-dihydrobenzoic acids[6a] led us to investigate the possibility of utilizing these materials for the preparation of cycloheptatrienes. The method we envisioned was to consist of (1) reduction of the dihydro acid with lithium aluminum hydride to a 1,4-dihydrobenzyl alcohol, (2) preparation of the corresponding p-toluenesulfonate derivative and (3) solvolysis of the sulfonate in acetic acid in the presence of a buffer, sodium dihydrogen phosphate monohydrate.[4d,e]

The solvolysis of 1,4-dihydrobenzyl p-toluenesulfonate (Ia) can lead theoretically to a number of products.[7] An SN2 displacement of the sulfonate group by solvent would give 1,4-dihydrobenzyl acetate (IIa) which may or may not react further under the conditions of the solvolysis. Reaction of Ia by an SN1 process would give the primary carbonium ion IIIa which can rearrange in a number of ways. Toluene could be formed by migration of hydride and aromatization of the resulting cation IVa or *via* protonation–deprotonation reactions of an intermediate methylenecyclohexadiene formed by loss of a proton from IIIa. A direct ring expansion of the ion IIIa would lead to the lower energy allylic carbonium ion VIa which, by loss of a proton, would give cycloheptatriene (VIIa). A more likely route to VIa would involve participation of the π-electrons of IIIa giving the homoallylic cation Va which can now expand to the cycloheptadienyl ion.[8] Still another route to cycloheptatriene could involve loss of a proton from the homoallylic cation

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(7) The formation of products is described in terms of discrete intermediates purely for the sake of clarity. It should be understood that some of the intermediates may not exist because of several steps occurring concertedly.

(8) This mode of reaction finds many analogies in the solvolysis of sulfonates and halides having γ,δ-unsaturation, the classical example being the conversion of cholesteryl p-toluenesulfonate to *i*-cholesteryl derivatives. See, for example, (a) M. Simonetta and S. Winstein, THIS JOURNAL, 76, 18 (1954); (b) E. M. Kosower and S. Winstein, *ibid.*, 78, 4347 (1956); (c) R. D. Haworth, J. McKenna and R. G. Powell, *J. Chem. Soc.*, 1110 (1953); (d) C. W. Shoppee, H. C. Richards and G. H. R. Summers, *ibid.*, 4817 (1956); (e) W. G. Dauben and G. J. Fonken, THIS JOURNAL, 78, 4736 (1956); (f) J. W. Rowe, A. Melera, D. Arigoni, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, 40, 1 (1957); and (g) P. Bruylants and A. Dewael, *Bull. Sci. Acad. Roy. Belg.* [V] 14, 140 (1928); *C. A.*, 22, 3883 (1928).