

**Preparation of 3,4-dichlorobenzyltriphenylsilane.** To 1.0 g. (0.042 g.-atom) of magnesium and 10 ml. of diethyl ether there was added dropwise with vigorous stirring a solution of 7.49 g. (0.038 mole) of 3,4-dichlorobenzyl chloride in 28 ml. of diethyl ether at a rate sufficient to maintain gentle refluxing. After 1 hr. of stirring, following completion of addition, acid titration<sup>25</sup> indicated a 90% yield of the Grignard reagent. The mixture was filtered under nitrogen into a stirred suspension of 10.90 g. (0.034 mole) of chlorotriphenylsilane in 25 ml. of diethyl ether. The resulting solution was stirred under reflux for 19 hr. before it was cooled and hydrolyzed. The aqueous layer was extracted with diethyl ether, and the combined organic solution was dried and evaporated. The residue was dissolved in boiling cyclohexane. Crystallization gave 3.95 g. (24.7%) of triphenylsilanol, m.p. 153–156° (mixed melting point). The filtrate was poured onto a column of dry alumina and eluted with cyclohexane to liberate a white solid, m.p. 107–110°. Recrystallization from cyclohexane gave 2.52 g. (15.7%) of 3,4-dichlorobenzyltriphenylsilane, m.p. 107–109°.

*Anal.* Calcd. for  $C_{26}H_{20}Cl_2Si$ : C, 71.58; H, 4.81; Si, 6.69. Found: C, 71.69, 71.53; H, 4.79, 4.68; Si, 6.78, 6.65.

(25) H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

**Preparation of 4-chlorobenzyltriphenylsilane.** To 1.0 g. (0.042 g.-atom) of magnesium and 10 ml. of diethyl ether there was added dropwise a solution of 6.70 g. (0.042 mole) of 4-chlorobenzyl chloride in 32 ml. of diethyl ether. The mixture was stirred for 3.5 hr. and then filtered into a solution of 12.2 g. (0.042 mole) of chlorotriphenylsilane in 40 ml. of tetrahydrofuran to give a semisolid mass. The addition of 50 ml. of tetrahydrofuran gave a suspension. After 1 hr. of stirring at room temperature, the suspension was hydrolyzed. The water layer was extracted with diethyl ether, and the combined organic solution was dried before being evaporated. The residue was dissolved in petroleum ether (b.p. 60–70°), and the solution was poured onto a column of dry alumina. Elution with the same solvent afforded 9.95 g. (62.5%) of 4-chlorobenzyltriphenylsilane, m.p. 116–118°. Recrystallization from petroleum ether (b.p. 60–70°) raised the melting point to 117–119°.

*Anal.* Calcd. for  $C_{25}H_{21}ClSi$ : C, 77.99; H, 5.49; Si, 7.29. Found: C, 78.24, 78.18; H, 5.36, 5.52; Si, 7.20, 6.98.

**Acknowledgment.** The authors are grateful to Oren L. Marrs for assistance.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## Synthesis of $\Delta^{8,9}$ - and $\Delta^{9,10}$ -Octal-1-one<sup>1</sup>

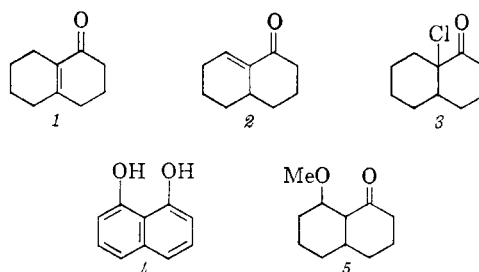
HERBERT O. HOUSE AND HUGH W. THOMPSON

Received March 16, 1961

Dehydrochlorination of the chloro ketone **6**, the predominant product obtained by chlorination of 1-decalone, afforded primarily  $\Delta^{9,10}$ -octal-1-one (**1**). Reaction of 1-decalone with mercuric acetate afforded a mixture of compounds **1**, **2**, **8**, **9**, **10**, and **11**, the predominant products resulting from attack at position 2. The enol acetates **14** and **15** were prepared. Reaction of **14** with peracetic acid followed by pyrolysis of the resulting acetoxy ketone **8** afforded a mixture of the octalones **1** and **2** in which the  $\Delta^{8,9}$ -isomer **2** predominated.

The chemical literature describes<sup>2–12</sup> a variety of reactions leading to a 1-octalone usually assigned the structure **1**. Although the chemical properties

of this substance were in accord with structure **1**, the observation<sup>5</sup> that this substance exhibited an ultraviolet absorption maximum at 243 m $\mu$  led Campbell and Harris to assign structure **2** to this ketone. The question was resolved by the subsequent synthesis<sup>12</sup> of both ketones **1** and **2**. The  $\Delta^{9,10}$ -isomer **1**, obtained by the dehydrohalogenation of one of the 9-chloro-1-decalones **3**<sup>12</sup> (cf. ref. 10), was found to be identical with the octalone previously described.<sup>2–11</sup> The  $\Delta^{8,9}$ -isomer



(1) This research has been supported by National Science Foundation Grant, No. G5107.

(2)(a) W. Hüchel, R. Danneel, A. Schwartz, and A. Gercke, *Ann.*, **474**, 121 (1929); (b) W. Hüchel and M. Blohm, *Ann.*, **502**, 114 (1933); (c) W. Hüchel and H. Naab, *Ann.*, **502**, 136 (1933).

(3)(a) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1637 (1935); (b) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 817 (1937).

(4) C. D. Nenitzescu and V. Przemetzky, *Ber.*, **74**, 676 (1941).

(5)(a) W. P. Campbell and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 2721 (1941); (b) G. C. Harris, *J. Am. Chem. Soc.*, **64**, 720 (1942).

(6) A. J. Birch, *J. Chem. Soc.*, 430 (1944).

(7) M. I. Bowman, C. C. Ketterer, and A. U. Chamberlain, *J. Org. Chem.*, **18**, 905 (1953).

(8) A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.*, **75**, 3717 (1953).

(9) K. Schenker and V. Prelog, *Helv. Chim. Acta*, **36**, 896 (1953).

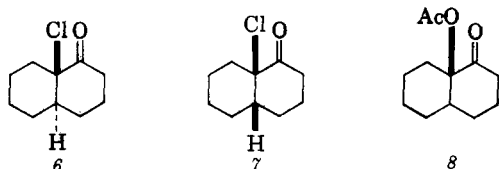
(10) H. E. Zimmerman and A. Mais, *J. Am. Chem. Soc.*, **81**, 3644 (1959).

(11)(a) R. K. Hill and R. T. Conley, *Chemistry and Industry*, 1314 (1956); (b) R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960).

(12) E. W. Warnhoff, Doctoral Dissertation, University of Wisconsin, 1953. In this investigation, reaction of the  $\Delta^{9,10}$ -isomer **1**, m.p.  $-15^{\circ}$  to  $-14^{\circ}$ , with ozone afforded  $\delta$ -keto-sebacic acid and the reaction of the  $\Delta^{8,9}$ -isomer **2**, m.p.  $-26^{\circ}$  to  $-24^{\circ}$ , with ozone yielded 1,4,7-tricarboxyheptane.

2, obtained from 1,8-dihydroxy naphthalene (4) via the intermediate methoxy ketone 5,<sup>12</sup> was found to be a new material.

As part of another study we desired syntheses capable of producing appreciable quantities of the octalones 1 and 2 and, accordingly, investigated various synthetic routes to these substances. Chlorination of 1-decalone with sulfuryl chloride<sup>12, 13</sup> afforded a crude liquid chloroketone from which the previously reported<sup>12</sup> crystalline chloro ketone 3, m.p. 40–41°, was isolated. Dehydrohalogenation of this crystalline chloro ketone 3 thermally, with collidine at 140° and with lithium chloride in dimethylformamide afforded mixtures of the octalones 1 and 2 containing 92%, 99%, and 99%, respectively, of the  $\Delta^{9,10}$ -isomer 1 in agreement with Warnhoff's work.<sup>12</sup> Comparable dehydrohalogenations of the crude liquid chloro ketone 3, which could be shown by infrared spectroscopy to contain neither of the octalones 1 or 2, afforded mixtures of the ketones 1 and 2 which contained from 78% to 90% of the  $\Delta^{9,10}$ -isomer 1. Subjecting mixtures of the unsaturated ketones 1 and 2 to the conditions of these dehydrohalogenations did not significantly alter the composition of these mixtures. We, therefore, conclude that the crude liquid chloro ketone 3 contains a small amount of a second stereoisomer of the crystalline compound, m.p. 40–41°, which yields significantly more, or perhaps exclusively, the octalone 2 on dehydrohalogenation. The requirement of a *trans*, coplanar transition state for at least the collidine dehydrohalogenation reaction<sup>14</sup> then permits the crystalline chloro ketone 3 to be assigned the *trans* stereochemistry indicated in structure 6. The ready conversion of the *trans* chloro ketone 6 to the octalone 1 is in agreement with the behavior of the corresponding bromo derivatives.<sup>10, 15</sup>



Thus the chloro ketone 6 provides a very satisfactory intermediate for synthesis of the  $\Delta^{9,10}$ -octalone 1 but is of no value for preparation of the  $\Delta^{8,9}$ -isomer 2. Since the recorded synthesis of the ketone 2 is particularly laborious, we were led to explore preparative methods for the acetoxy ketones 3, particularly the isomer with a *trans*

(13) E. W. Warnhoff and W. S. Johnson, *J. Am. Chem. Soc.*, **75**, 494 (1953).

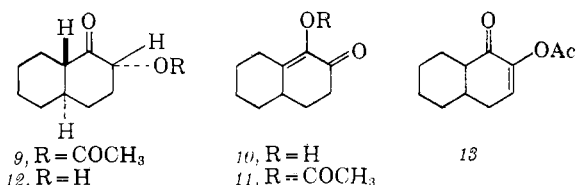
(14) For a discussion see H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *J. Am. Chem. Soc.*, **82**, 1457 (1960), and ref. 10.

(15) The published information (ref. 10) concerning the dehydrohalogenation of the bromo analog of the *cis* chloro ketone 7 does not establish which of the octalones 1 or 2 was being formed.

ring fusion, since pyrolysis of this substance would be expected<sup>16</sup> to yield the  $\Delta^{8,9}$ -isomer 2.

The first reaction explored was that of 1-decalone with mercuric acetate.<sup>17</sup> From a typical experiment, the products formed (estimated by gas chromatography) were the  $\Delta^{9,10}$ -octalone 1 (2%), the  $\Delta^{8,9}$ -octalone 2 (12%), an unstable component believed to be the acetoxy decalone 8 (14%), a 2-acetoxy-1-decalone believed to possess the stereochemistry represented in structure 9 (29%), the enol 10 of decalin-1,2-dione (18%) and the corresponding enol acetate 11 (13%).

The acetoxy ketone 9 was hydrolyzed to the hydroxy ketone 12 which was oxidized with bismuth triacetate<sup>18</sup> to the enolic diketone 10. Acetylation of this diketone produced the enol acetate 11. The NMR spectrum (40 mc.) of the acetoxy ketone 9 contains a multiplet centered at 5.03  $\tau$  attributable to the single hydrogen atom at position 2 in structure 9. The ultraviolet spectrum of 9 exhibits a maximum at 284.5  $m\mu$  ( $\epsilon$  29) compared with a value of 286.5 ( $\epsilon$  27) for *trans*-1-decalone indicating the location of the 2-acetoxy function in an equatorial conformation.<sup>19</sup> Based on the assumption that this substance, formed under equilibrating conditions, has the more stable *trans* ring fusion, the stereochemistry indicated in structure 9 has been assigned to this acetoxy ketone. Similarly, the ultraviolet absorption of the hydroxy ketone 12 at 275  $m\mu$  ( $\epsilon$  38) suggests that this substance possesses the most stable stereochemical arrangement depicted in structure 12.



The ultraviolet absorption, 243.5  $m\mu$  ( $\epsilon$  14,100), of the enol acetate derived from the  $\alpha$ -diketone 10 indicated that the substance possesses structure 11 rather than 13.<sup>20</sup> Similarly, the ultraviolet absorption of the diketone at 276.5  $m\mu$  ( $\epsilon$  10,200) is in accord with the direction of enolization indicated in structure 10.

Our efforts to isolate a pure sample of the 9-acetoxy ketone 8 were complicated by the ready

(16) For a discussion of steric requirements in this olefin-forming reaction see C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

(17)(a) W. Treibs and H. Bast, *Ann.*, **561**, 165 (1948); (b) W. Treibs, G. Lucius, H. Kogler, and H. Breslauer, *Ann.*, **581**, 59 (1953); (c) P. R. Jefferies, A. K. Macbeth, and B. Milligan, *J. Chem. Soc.*, 705 (1954).

(18) W. Rigby, *J. Chem. Soc.*, 793 (1951).

(19) L. F. Fieser and M. Fieser, *Steroids*, Reinhold Publishing Corp., New York, N. Y., 1959, pp. 175–176.

(20)(a) L. F. Fieser and R. Stevenson, *J. Am. Chem. Soc.*, **76**, 1728 (1954); (b) L. F. Fieser and M. Fieser, *Natural Products Related to Phenanthrene*, 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 195–197.

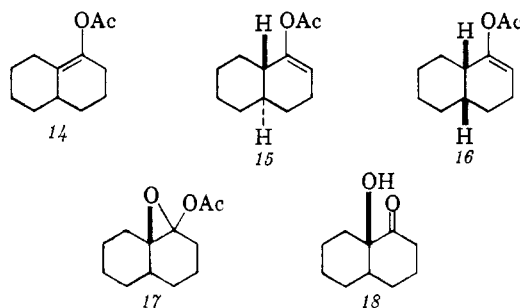
thermal decomposition of the material to form the octalones 1 and 2. Consequently, a pure sample of the acetoxy ketone 8 was not isolated.

It seems likely that both stereoisomers of structure 8 were present. Thus, the reaction of 1-decalone with mercuric acetate afforded primarily products resulting from attack at the methylene group (position 2) rather than at the methinyl group (position 9), an observation in accord with the reported<sup>17</sup> reaction of menthone with mercuric acetate at the less highly substituted position.

In order to introduce functionality only at the 9 position of 1-decalone, we sought to prepare the enol acetate 14. The reaction of 1-decalone with acetic anhydride in the presence of *p*-toluenesulfonic acid has been reported<sup>10</sup> to yield the enol acetate 14; however, the homogeneity of this product was not established. Repetition of this experiment afforded a mixture of enol acetates containing the desired product 14 (90%), the  $\Delta^{1,2}$ -isomer 15 (5%) and an additional component (3%) believed to be the *cis*- $\Delta^{1,2}$ -compound 16. The reaction of 1-decalone with isopropenyl acetate in the presence of *p*-toluenesulfonic acid<sup>21,22</sup> yielded a mixture containing approximately equal amounts of each of the two enol acetates 14 and 15 as well as small amounts of the product 16 and the starting material.

The ultraviolet spectrum of the  $\Delta^{9,1}$ -enol acetate 14 has a molecular extinction coefficient of 4400 at 210  $m\mu$  in agreement with presence of a tetra-substituted double bond.<sup>23</sup> The NMR spectrum (60 mc.) of the product exhibits no absorption below 7.35  $\tau$  indicating the absence of vinyl hydrogen atoms. The  $\Delta^{1,2}$  isomer 15 has a molecular extinction coefficient of 1900 at 210  $m\mu$  (trisubstituted double bond<sup>23</sup>) with NMR absorption (60 mc.) centered at 4.83  $\tau$  (unresolved peak) attributable to a vinyl hydrogen atom. We were unable to isolate a sufficient quantity of the component, believed to be the enol acetate 16, to permit characterization. Since the enol acetates were prepared from *trans*-1-decalone, the predominant  $\Delta^{1,2}$ -enol acetate has been assigned the *trans* configuration 15.<sup>24</sup> Our results are in agreement with the previous generalization<sup>21,22,25</sup> that the more highly

substituted enol acetate is obtained by use of acetic anhydride whereas use of isopropenyl acetate affords substantial amounts of the less highly substituted isomer. Reaction of the enol acetate 14



with peracetic acid followed by pyrolysis of the crude acetoxy ketones 8, presumably formed *via* the epoxy acetate 17,<sup>25,26</sup> afforded a mixture containing the octalones 1 and 2 in a ratio of 1 to 5 as well as 1-decalone and its enol acetates. Hydrolysis of the mixture to convert the enol acetates to 1-decalone followed by fractional distillation afforded the desired octalones 1 and 2. Acid hydrolysis of the crude acetoxy ketone 8 obtained from the enol acetate 14 afforded a crystalline hydroxy ketone, believed to be one of the stereoisomers of structure 18, in low yield.

The NMR spectrum (60 mc.) of the  $\Delta^{8,9}$ -octalone 2 exhibits a doublet (or partially resolved quartet) centered at 3.43  $\tau$  attributable to a vinyl hydrogen atom whereas the spectrum (60 mc.) of the  $\Delta^{9,10}$ -isomer 1 exhibits no absorption below 7  $\tau$ . Other properties of 1 and 2 are cited in the experimental section of this paper.

#### EXPERIMENTAL<sup>27</sup>

*9-Chloro-trans-1-decalone* (6). A solution of 39.1 g. (0.247 mole) of *trans*-1-decalone<sup>28</sup> in 185 ml. of carbon tetrachloride was kept at 19° to 26° while a solution of 39.2 g. (0.290 mole) of sulfuryl chloride in 100 ml. of carbon tetrachloride

(26)(a) N. S. Leeds, L. K. Fukushima, and T. F. Gallagher, *J. Am. Chem. Soc.*, **76**, 2943 (1954); (b) W. S. Johnson, B. Gastambide, and R. Pappo, *J. Am. Chem. Soc.*, **79**, 1991 (1957).

(27) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Baird, Model B, or a Perkin-Elmer, Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11MS. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

(28) The *trans*-1-decalone was prepared by the procedure of W. G. Dauben, R. C. Tweit, and C. Mannerskantz [*J. Am. Chem. Soc.*, **76**, 4420 (1954)]. Gas chromatographic analysis (ref. 30) of our material, b.p. 87–91° (6 mm.),  $n_D^{25}$  1.4846, indicated the presence of 84% *trans*-1-decalone, 14% *cis*-1-decalone and 2% of a mixture of tetralin and the decalins. The reported values [C. D. Gutsche and H. H. Peter, *J. Am. Chem. Soc.*, **77**, 5971 (1955)] for the *cis* isomer are b.p. 120–121° (20 mm.),  $n_D^{25}$  1.4910, and for the *trans* isomer  $n_D^{25}$  1.4852.

(21) R. B. Moffett and D. I. Weisblat, *J. Am. Chem. Soc.*, **74**, 2183 (1952).

(22) H. Vanderhaeghe, E. R. Katzenellenbogen, K. Dobriner, and T. F. Gallagher, *J. Am. Chem. Soc.*, **74**, 2810 (1952).

(23) L. F. Fieser and M. Fieser, *Steroids*, Reinhold Publishing Corp., New York, N. Y., 1959, p. 174.

(24) The recently reported [C. Djerassi and J. Staunton, *J. Am. Chem. Soc.*, **83**, 736 (1961)] conversion of *cis*-1-decalone to a mixture of the  $\Delta^{1,9}$ -enol acetate 14 and the *cis*- $\Delta^{1,2}$ -enol acetate 16 under conditions comparable to those employed in our work indicates that these reaction conditions acetylate the  $\Delta^{1,2}$ -enol more rapidly than the *cis*-1-decalone is isomerized to the more stable *trans* isomer.

(25) A. H. Soloway, W. J. Considine, D. K. Fukushima, and T. F. Gallagher, *J. Am. Chem. Soc.*, **76**, 2941 (1954); (b) C. W. Marshall, T. H. Kritchevsky, S. Lieberman, and T. F. Gallagher, *J. Am. Chem. Soc.*, **70**, 1837 (1948).

was added, dropwise and with stirring over a period of 65 min. The resulting solution was stirred for 2 hr. and then washed successively with water, aqueous sodium bicarbonate, and aqueous sodium chloride. After the organic solution had been dried<sup>29</sup> and concentrated, a gas chromatogram<sup>30</sup> of the residual oil indicated the presence of 8% of the unchanged decalone and 91% of a second component. A portion of this material was distilled under reduced pressure and the product collected, b.p. 65–79° (0.6 mm.)  $n_D^{25}$  1.5038, [lit.,<sup>12</sup> b.p., 82–83° (2 mm.)  $n_D^{25}$  1.5030–1.5036] was partially crystallized by cooling. Two recrystallizations of this material from petroleum ether afforded the pure chloro ketone as white prisms melting at 40–41° (lit.,<sup>12</sup> m.p., 39.7–40.2°),  $n_D^{25}$  (supercooled) 1.5013, with infrared absorption<sup>31</sup> at 1718 cm.<sup>-1</sup> (C=O, the corresponding band in 1-decalone is found at 1708 cm.<sup>-1</sup>) and an ultraviolet maximum<sup>32</sup> at 300.5 m $\mu$  ( $\epsilon$  45) [lit.,<sup>12</sup> 299 m $\mu$  ( $\epsilon$  48)]. The corresponding band in *trans*-1-decalone is at 286.5 m $\mu$  ( $\epsilon$  26.6).

*Dehydrochlorination of the chloro ketone 6. (A) Thermal.* A 1.001-g. (5.36 mmoles) sample of the pure chloro ketone **6** was heated to 185° for 10 min. under a nitrogen atmosphere and then cooled and distilled under reduced pressure (7 mm.) in a short path still. Analysis of the distillate, 0.4904 g. (61%) of a yellow liquid, by gas chromatography<sup>33</sup> indicated the presence of 87%  $\Delta^9,10$ -octal-1-one and 8% of  $\Delta^8,9$ -octal-1-one. Samples collected from the chromatogram<sup>33</sup> were identified by comparison of their infrared spectra with the spectra of authentic samples.

(B) *With collidine.* A mixture of 0.9995 g. (5.36 mmoles) of the pure chloro ketone **6** and 0.72 g. (5.9 mmoles) of  $\gamma$ -collidine was heated to 143° for 8 min. under a nitrogen atmosphere. The resulting mixture was diluted with petroleum ether, filtered to separate 0.8290 g. (98%) of  $\gamma$ -collidine hydrochloride and then washed successively with 4% aqueous hydrochloric acid, aqueous sodium bicarbonate, and water. The organic layer was concentrated and distilled under reduced pressure (0.4 mm.) in a short path still to separate 0.712 g. (89%) of a yellow liquid which contained<sup>33</sup> 99% of  $\Delta^9,10$ -octal-1-one (identified from the infrared spectrum of a sample collected from the gas chromatograph<sup>33</sup>) and <1%  $\Delta^8,9$ -octal-1-one.

(C) *With lithium chloride and dimethylformamide.* A solution of 1.004 g. (5.36 mmoles) of the pure chloro ketone **6** and 2.27 g. (0.0536 mole) of lithium chloride in 14 ml. of dimethylformamide was heated to 120° for 5 hr. while a slow stream of nitrogen was bubbled through the solution. The resulting mixture was diluted with water and extracted with petroleum ether after which the extract was washed with water, concentrated, and distilled under reduced pressure in a short path still. The distillate, 0.6930 g. (86%) of a colorless liquid contained<sup>33</sup> 99% of  $\Delta^9,10$ -octal-1-one, identified as previously described, and 1% of  $\Delta^8,9$ -octal-1-one.

(D) *Dehydrochlorination of the crude chloro ketone.* Application of the aforementioned dehydrohalogenation procedures to the crude, liquid chloro ketone afforded mixtures in which the proportions<sup>33</sup> of the octalones were as follows: thermal dehydrochlorination, 78%  $\Delta^9,10$ -octal-1-one, 22%  $\Delta^8,9$ -octal-1-one; collidine dehydrochlorination, 89%  $\Delta^9,10$ -octal-1-one; 11%  $\Delta^8,9$ -octal-1-one; lithium chloride-dimethylformamide dehydrochlorination, 90%  $\Delta^9,10$ -octal-1-one, 10%  $\Delta^8,9$ -octal-1-one.

*Reaction of trans-1-decalone with mercuric acetate.* A mixture of 37.35 g. (0.245 mole) of *trans*-1-decalone, 109 g. (0.342 mole) of mercuric acetate and 128 g. of acetic acid

was heated to boiling, a voluminous precipitate separating at approximately 100°. Sufficient acetic acid was permitted to distil from the reaction mixture so that the temperature of the boiling solution reached 130° at which time the mixture was refluxed for 1.5 hr. After the resulting reaction mixture had been cooled, gas chromatographic analysis<sup>30</sup> of the crude product suggested the presence of the following high-boiling components: *trans*-1-decalone (12%), the  $\Delta^8,9$ -octalene **2** (12%), the  $\Delta^9,10$ -octalene **1** (2%), the  $\alpha$ -diketone **10** (18%), a component believed to be the 9-acetoxy ketone **8** (14%), the 2-acetoxy ketone **9** (29%), and the enol acetate **11** (13%). After an ether solution of the crude product had been washed with aqueous sodium bicarbonate, dried<sup>29</sup> and concentrated, distillation of the residue afforded 35.2 g. of the mixture of products, b.p. 55–111° (0.5 mm.). A 26.9-g. portion of this distillate was fractionally distilled through a 40-cm. spinning band column to effect partial separation of the components present. The  $\Delta^9,10$ -octalene **1** and the  $\Delta^8,9$ -octalene **2**, collected from the gas chromatographs<sup>34</sup> of appropriate fractions were shown to be identical with subsequently described samples by comparison of the infrared and ultraviolet spectra of the materials.

A total of 0.3826 g. of the crude *decalin-1,2-dione 10*, m.p. 85–87.5°, was separated from appropriate fractions by fractional crystallization. Recrystallization from petroleum ether afforded the pure enolic diketone as colorless, diamond-shaped platelets, m.p. 87.5–88°, which gave a purple-brown color with ethanolic ferric chloride and were soluble in aqueous sodium hydroxide. The compound has an ultraviolet absorption maximum<sup>32</sup> at 276.5 m $\mu$  ( $\epsilon$  12,000) with infrared absorption<sup>31</sup> at 3440 cm.<sup>-1</sup> (assoc. O–H), 1670 cm.<sup>-1</sup> (conj. C=O) and 1645 cm.<sup>-1</sup> (conj. C=C).

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>: C, 72.26; H, 8.49. Found: C, 72.35; H, 8.52.

A sample of the enol acetate **11**, collected from gas chromatograms<sup>34</sup> of the appropriate fractions, was shown to be identical with a subsequently described sample by comparison of the infrared and ultraviolet spectra of the compounds. Fractional crystallization of appropriate fractions separated 3.0351 g. of the crude 2-acetoxy ketone **9**, m.p. 69.5–73°. Recrystallization from petroleum ether afforded the pure acetoxy ketone as white needles, m.p. 72.5–73.5°, with an ultraviolet maximum<sup>32</sup> at 284.5 m $\mu$  ( $\epsilon$  29.3) and infrared absorption<sup>31</sup> at 1740 cm.<sup>-1</sup> (ester C=O) and 1730 cm.<sup>-1</sup> (C=O). The NMR spectrum (40 mc.)<sup>31</sup> exhibits a multiplet centered at 5.03  $\tau$  [—CO—CH(OAc)CH<sub>2</sub>—] with a singlet at 7.93  $\tau$  (CH<sub>3</sub>—COO—) and an envelope of unresolved absorption bands in the region 7.5 to 9.1  $\tau$  (—CH<sub>2</sub>—).

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>: C, 68.54; H, 8.63. Found: C, 68.54; H, 8.77.

A mixture of 2.0832 g. (9.95 mmoles) of the 2-acetoxy ketone **9**, 21 ml. of 5% aqueous sulfuric acid, and sufficient dioxane to obtain a homogeneous solution was refluxed for 1 hr. and then cooled, neutralized with aqueous sodium bicarbonate, and extracted with petroleum ether. After the extract had been concentrated and cooled, 1.0843 g. (65%) of the crude *2-hydroxy ketone 12*, m.p. 60–76°, separated. Recrystallization afforded the pure hydroxy ketone as white prisms, m.p. 76–76.7°, with an ultraviolet maximum<sup>32</sup> at 275 m $\mu$  ( $\epsilon$  38) and infrared bands<sup>31</sup> at 3540 cm.<sup>-1</sup> (O—H) and 1712 cm.<sup>-1</sup> (C=O).

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: C, 71.39; H, 9.59. Found: C, 71.13; H, 9.67.

A mixture of 100 mg. (0.595 mmole) of the 2-hydroxy ketone **12**, 230 mg. (0.595 mmole) of bismuth triacetate,<sup>18</sup> and 0.6 ml. of acetic acid was heated to 100° for 20 min. and then to 110° for 75 min. at which time the ultraviolet spectrum of the reaction mixture indicated that oxidation

(34) A column packed with Carbowax 600 partially esterified with phthalic acid suspended on ground firebrick was employed.

(29) Magnesium sulfate was employed as a drying agent.

(30) A column packed with Dow Silicone Fluid No. 710 suspended on ground firebrick was employed.

(31) Determined in carbon tetrachloride solution.

(32) Determined in 95% ethanol solution.

(33) A column packed with Carbowax 1540 partially esterified with phthalic acid suspended on ground firebrick was employed.

was complete. The reaction mixture was cooled, diluted with petroleum ether and acetone, and filtered. The filtrate was neutralized with sodium bicarbonate and concentrated. Sublimation of the residue afforded 72 mg. (72%) of the crude diketone 10, m.p. 68–81°. Recrystallization afforded 28.3 mg. (28%) of the pure diketone 10, m.p. 84–86°, shown to be identical with the previously described sample by a mixed melting point determination and by comparison of the infrared and ultraviolet spectra of the two samples.

A solution of 0.500 g. (3.01 mmoles) of the  $\alpha$ -diketone 10 and 5.3 g. (43 mmoles) of acetic anhydride in 10 ml. of pyridine was allowed to stand for 4 days and then diluted with ether and washed with aqueous sodium bicarbonate and with water. The ethereal solution was dried,<sup>29</sup> concentrated, and distilled under reduced pressure (0.3 mm.) in a short path still (pot temperature 105–130°) to separate 0.466 g. (74%) of the enol acetate 11 as a pale yellow liquid,  $n_D^{25}$  1.5114. The product exhibits ultraviolet absorption<sup>32</sup> at 243.5  $m\mu$  ( $\epsilon$  14,100) with infrared bands<sup>31</sup> at 1767  $cm^{-1}$  (enol ester C=O) and 1688  $cm^{-1}$  (conj. C=C).

Anal. Calcd. for  $C_{12}H_{18}O_2$ : C, 69.21; H, 7.74. Found: C, 68.96; H, 7.65.

**Reaction of *trans*-1-decalone with isopropenyl acetate.** A mixture of 15.22 g. (0.10 mole) of *trans*-1-decalone, 20 g. (0.20 mole) of isopropenyl acetate, and 0.10 g. of *p*-toluenesulfonic acid was heated to such a temperature that a mixture of acetone and some isopropenyl acetate continuously distilled from the mixture. At the end of 6.5 hr. an additional 7 g. of isopropenyl acetate was added and heating was continued for 13.5 hr. at which time the temperature of the reaction mixture was raised to expel all the acetone. The reaction mixture was cooled, diluted with ether, and washed with aqueous sodium bicarbonate. After the ethereal solution had been dried<sup>29</sup> and concentrated, gas chromatographic analysis<sup>35</sup> indicated the presence of unchanged 1-decalone (2%), the  $\Delta^{9,1}$ -enol acetate 14 (44%), the *trans*- $\Delta^{1,2}$ -enol acetate 15 (46%) and a component believed to be the *cis*- $\Delta^{1,2}$ -enol acetate 16 (7%). Distillation of the crude material afforded 14.33 g. (74%) of a mixture of the enol acetates, b.p. 68–76° (0.6 mm.). A sample of the *trans*- $\Delta^{1,2}$ -enol acetate 15, collected from the gas chromatograph<sup>35</sup> of the mixture, was further purified by distillation under reduced pressure in a short path still. The liquid product,  $n_D^{25}$  1.4847, exhibits infrared bands<sup>31</sup> at 1750  $cm^{-1}$  (enol ester C=O) and 1678  $cm^{-1}$  (C=C) with a molecular extinction coefficient of 1900 at 210  $m\mu$  in the ultraviolet.<sup>32</sup> The NMR spectrum (60 mc.)<sup>31</sup> of the substance exhibits a multiplet centered at 4.83  $\tau$  (—C=CH—), a singlet at 7.98  $\tau$  ( $CH_2COO$ —) and broad, unresolved absorption in the region 7.60 to 9.35  $\tau$  (— $CH_2$ —).

Anal. Calcd. for  $C_{12}H_{18}O_2$ : C, 74.19; H, 9.34. Found: C, 74.43; H, 9.47.

The  $\Delta^{9,1}$ -enol acetate 14 collected from the chromatograph<sup>35</sup> was shown to be identical with the subsequently described sample by comparison of the infrared and ultraviolet spectra of the two samples.

**Reaction of *trans*-1-decalone with acetic anhydride.** A mixture of 62.8 g. (0.396 mole) of *trans*-1-decalone, 130 g. (1.23 moles) of acetic anhydride and 1.0 g. of *p*-toluenesulfonic acid was heated under partial reflux in such a way that acetic acid was allowed to distil from the reaction mixture. After 6 hr., at which time 55 ml. of distillate had been collected, an additional 50 ml. of acetic anhydride was added and the process was continued for an additional 3.5 hr. At this time 1.0 g. of anhydrous potassium acetate was added and the mixture was cooled, diluted with petroleum ether, and washed with aqueous sodium bicarbonate. The organic layer was concentrated and distilled to separate 75.6 g. (96%) of a mixture of enol acetates as a colorless liquid, b.p. 68–79° (0.6 mm.),  $n_D^{25}$  1.4870–1.4880.<sup>36</sup> Gas chromatographic analysis<sup>35</sup> indicated the presence of the  $\Delta^{9,1}$ -enol

acetate 14 (90%), the *trans*- $\Delta^{1,2}$ -enol acetate 15 (5%), a component believed to be the *cis*- $\Delta^{1,2}$ -enol acetate 16 (3%) and traces of decalone and tetralin (present in the starting material). A sample of the  $\Delta^{9,1}$ -enol acetate 14, collected from the gas chromatograph,<sup>35</sup> was redistilled under reduced pressure in a short path still. The liquid product,  $n_D^{25}$  1.4881, has infrared absorption<sup>31</sup> at 1750  $cm^{-1}$  (enol ester C=O) and at 1695  $cm^{-1}$  (C=C) with a molecular extinction coefficient of 4400 at 210  $m\mu$  in the ultraviolet.<sup>32</sup> The NMR spectrum (60 mc.)<sup>31</sup> of the material exhibits a peak at 8.07  $\tau$  ( $CH_2COO$ ) with broad, unresolved absorption in the region 7.35 to 9.25  $\tau$  (— $CH_2$ —) and no absorption attributable to vinyl hydrogen atoms.

Anal. Calcd. for  $C_{12}H_{18}O_2$ : C, 74.19; H, 9.34. Found: C, 74.00; H, 9.37.

**Reaction of 1-acetoxy- $\Delta^{1,9}$ -octalin (14) with peracetic acid.** A mixture of 75.6 g. (0.39 mole) of the crude  $\Delta^{1,9}$ -enol acetate 14 (obtained from the previously described reaction of 1-decalone with acetic anhydride), 175 ml. (0.92 mole) of a 40% solution of peracetic acid in acetic acid, 100 g. (0.735 mole) of sodium acetate trihydrate, 150 ml. of water, and 1000 ml. of petroleum ether was stirred at room temperature for 11 hr. An additional 50 ml. (0.26 mole) of 40% peracetic acid in acetic acid was added and stirring was continued for 13 hr. The excess peracetic acid was reduced by the addition, slowly and with cooling, of 155 g. of sodium sulfite. After the acetic acid had been neutralized by the addition of sodium bicarbonate, the organic layer was separated and concentrated. Gas chromatographic analysis<sup>30</sup> of the residue indicated the presence of 83% of a new component (or components) accompanied by the unchanged enol acetates 14, 15, and 16. After collection<sup>30</sup> of the peak corresponding to the major component (or components), subsequent analysis<sup>30</sup> indicated that, after collection, this component was contaminated with 15–20% of the  $\Delta^{8,9}$ -octalone 2. The infrared spectrum<sup>31</sup> of the collected sample exhibits peaks at 1737  $cm^{-1}$  (ester C=O) and 1721  $cm^{-1}$  (C=O) as well as low-intensity peaks at 1688 and 1620  $cm^{-1}$  attributable to the  $\Delta^{8,9}$ -octalone 2. After samples of this material had been heated to approximately 250° for 5–10 min., the major components present were the  $\Delta^{8,9}$ -octalone 2 and the  $\Delta^{9,10}$ -octalone 1 in ratios greater than two to one.

A mixture of 3.774 g. of the crude 9-acetoxy-1-decalone 8 (obtained by reaction of the crude enol acetate 14 with peracetic acid), 35 ml. of 5% aqueous sulfuric acid and sufficient dioxane to effect homogeneity was refluxed for 100 min. and then cooled and extracted with petroleum ether. After the extract had been concentrated and cooled, the solid which separated was recrystallized from petroleum ether to afford 0.1420 g. of a hydroxy ketone as colorless prisms, m.p. 62–63°. An additional crystallization raised the melting point of the material to 62.5–63.5°, yield 73.2 mg. The substance, which exhibits infrared absorption<sup>31</sup> at 3520  $cm^{-1}$  (OH) and 1708  $cm^{-1}$  (C=O) and an ultraviolet maximum<sup>32</sup> at 287.5  $m\mu$  ( $\epsilon$  34.5), has been tentatively assigned the 9-hydroxy-1-decalone structure 18 although the possibility that the material is a 2-hydroxy-1-decalone stereoisomeric with 18 has not been excluded.

Anal. Calcd. for  $C_{10}H_{16}O_2$ : C, 71.39; H, 9.59. Found: C, 71.27; H, 9.56.

**Pyrolysis of crude 9-acetoxy-1-decalone (8).** An 82.335-g. sample of the crude product obtained from reaction of the enol acetate 14 with peracetic acid was pyrolyzed in two equal portions at 220–225° for 70 min. The pyrolyses were conducted in a flask fitted with a distillation head and a gas inlet to permit nitrogen to bubble slowly through the reaction mixture during the pyrolysis. The combined materials (distillates and residues) from the pyrolyses were neutralized by the addition of aqueous sodium bicarbonate and then extracted with petroleum ether. The organic

(35) A column packed with Dow Silicone Fluid No. 550 suspended on ground firebrick was employed.

(36) The previously reported (ref. 10) product, b.p. 63–66° (0.75 mm.) is presumably similar in composition to our material.

extract was concentrated and distilled to separate 24.947 g. of clear distillate, b.p. 67–79° (0.6 mm.). The residue, 33.249 g., was again subjected to a similar pyrolysis and isolation procedure to afford an additional 14.425 g. of distillate, b.p. 68–80° (0.6 mm.). Gas chromatographic analysis<sup>33</sup> of the combined distillates indicated the presence of the octalones 1 and 2 in a ratio of 1 to 5 as well as decalone and its enol acetates. A mixture of the combined distillates (39.371 g.), 200 ml. of 5% aqueous sulfuric acid, and sufficient dioxane to effect homogeneity was refluxed for 1.5 hr. and then cooled, neutralized with aqueous sodium bicarbonate, and extracted with petroleum ether. After the organic extract had been concentrated, distillation of the residue afforded 31.462 g. of colorless distillate, b.p. 60–74° (0.65 mm.), which contained<sup>33</sup> tetralin (~1%), 1-decalone (17%), the  $\Delta^{8,9}$ -octalone 2 (64%), the  $\Delta^{9,10}$ -octalone 1 (12%), and a number of minor components (total 6%). Fractional distillation through a 90-cm. spinning-band column served to separate the mixture into fractions containing primarily each of the three main components. The fractions containing high concentrations of the  $\Delta^{8,9}$ -octalone 2 were collected in the range 53–58° (0.08 mm.),  $n_D^{25}$  1.5156–1.5166.

$\Delta^{8,9}$ -Octal-1-one (2). A sample of this ketone, collected from the gas chromatographs<sup>33</sup> of appropriate fractions, was redistilled under reduced pressure in a short path still to obtain a sample of the ketone, a colorless liquid  $n_D^{27}$  1.5157 (lit.,<sup>12</sup>  $n_D^{25}$  1.5161), whose purity was greater than 95% the principal contaminant being the isomeric octalone 1. The product exhibits infrared absorption<sup>31</sup> at 1678 cm.<sup>-1</sup> (conj. C=O) and 1623 cm.<sup>-1</sup> (conj. C=C) with an ultraviolet maximum<sup>32</sup> at 246 m $\mu$  ( $\epsilon$  6170) [lit.,<sup>12</sup> 246 m $\mu$  ( $\epsilon$  7300)] The infrared spectrum<sup>37</sup> of the material is identical with the

(37) Determined as a solution in chloroform.

spectrum of the sample prepared previously.<sup>12</sup> The NMR spectrum (60 mc.)<sup>38</sup> exhibits a doublet (or a partially resolved

quartet) centered at 3.43  $\tau$  (C=CH—CH<sub>2</sub>—) with intense,

partially resolved absorption in the region 7.20 to 9.25  $\tau$  (—CH<sub>2</sub>—). Reaction of a 19.6-mg. sample of the ketone with 2,4-dinitrophenylhydrazine yielded, after several recrystallizations from ethanol-ethyl acetate mixtures, the 2,4-dinitrophenylhydrazone as deep red needles, m.p. 226–226.5° dec. [lit.,<sup>12</sup> m.p. 223.5–224° dec.], yield 17 mg. (38%). Reaction of a 35-mg. sample of the ketone with semicarbazide yielded, after several crystallizations from aqueous ethanol, 8 mg. (15%) of the semicarbazone as white crystals, m.p. 197.5–199.5° dec. [lit.,<sup>12</sup> m.p., 197.5–198.5° dec.].

$\Delta^{9,10}$ -Octal-1-one (1). A sample of this ketone, collected from gas chromatographs<sup>34</sup> of appropriate fractions and distilled under reduced pressure in a short path still, was obtained as a colorless liquid  $n_D^{25}$  1.5267 (lit.<sup>12</sup>  $n_D^{25}$  1.5263), whose purity was approximately 95%, the principal contaminant being the octalone 2. The material has infrared absorption<sup>31</sup> at 1664 cm.<sup>-1</sup> (conj. C=O) and 1634 cm.<sup>-1</sup> (conj. C=C) with an ultraviolet maximum<sup>32</sup> at 245.5 m $\mu$  ( $\epsilon$  12,400) [lit.,<sup>12</sup> 245 m $\mu$  ( $\epsilon$  12,300)]. The NMR spectrum (60 mc.)<sup>38</sup> of the ketone has a series of partially resolved bands in the region 7.45 to 8.65  $\tau$  (—CH<sub>2</sub>—) with no absorption attributable to a vinyl hydrogen atom. Reaction of a 15.5-mg. sample of the ketone with 2,4-dinitrophenylhydrazine yielded, after several recrystallizations from an ethanol-ethyl acetate mixture, 26.5 mg. (80%) of the 2,4-dinitrophenylhydrazone as red needles m.p. 266–266.5° dec. [lit., m.p. 264.5–265.5°,<sup>11</sup> 264–266°,<sup>9</sup> 265.5–266° dec.<sup>12</sup>].

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(38) Determined as a solution in deuteriochloroform.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

## Synthesis of 1,2,3,4-Tetramethylcyclopentanes. I<sup>1,2</sup>

HAROLD N. MILLER<sup>3</sup> AND KENNETH W. GREENLEE

Received March 20, 1961

Synthesis of none of the six isomeric 1,2,3,4-tetramethylcyclopentanes has previously been reported, though one of them (1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclopentane) has been found in a crude petroleum. Now, three have been synthesized by methods which clearly establish their configurations; they are 1-*cis*-2-*cis*-3-*cis*-4- and 1-*trans*-2-*trans*-3-*cis*-4- and 1-*cis*-2-*trans*-3-*cis*-4-tetramethylcyclopentane. The three geometrically isomeric 2,3-dimethyl-5-norbornenes were oxidized to three dimethylcyclopentanedicarboxylic acids, which were reduced in four steps to tetramethylcyclopentanes of high purity. Their properties compare reasonably well with the predicted values.

The tetramethylcyclopentanes include seven structural isomers, or sixteen geometric isomers of which only seven have been synthesized<sup>4,5</sup> and four of these were obtained as pairs which were not separated and characterized. One of the structural isomers, 1,2,3,4-tetramethylcyclopentane has six

(1) This paper is based on the Ph.D. thesis of Harold N. Miller, The Ohio State University, 1959.

(2) Financial support for this research was provided by the American Petroleum Institute Research Projects 45 and 58A.

(3) Present address: Esso Research and Engineering Co., Linden, N. J.

(4) G. Slomp, M. Inatome, C. E. Bowers, J. M. Derfer, K. W. Greenlee, and C. E. Boord, *J. Org. Chem.*, **25**, 514 (1960).

(5) J. F. Eykman, *Chem. Weekblad*, **3**, 685 (1906).

possible geometric isomers representing an especially difficult problem in synthesis and identification: A. 1-*cis*-2-*cis*-3-*cis*-4-Tetramethylcyclopentane; B. 1-*cis*-2-*cis*-3-*trans*-4-Tetramethylcyclopentane; C. 1-*cis*-2-*trans*-3-*cis*-4-Tetramethylcyclopentane; D. 1-*cis*-2-*trans*-3-*trans*-4-Tetramethylcyclopentane; E. 1-*trans*-2-*cis*-3-*trans*-4-Tetramethylcyclopentane; F. 1-*trans*-2-*trans*-3-*cis*-4-Tetramethylcyclopentane. Only one of these (E) has been characterized<sup>6</sup> and it was not synthesized but isolated from petroleum.

The present paper is a report on the stereospecific synthesis of three of these hydrocarbons, A, C, and

(6) M. B. Epstein, C. B. Willingham, B. J. Mair, and F. D. Rossini, *Anal. Chem.*, **28**, 1924 (1956).