

2. Preparation of α,α -Difluoroglutaric Acid by Hydrolysis of 2-Chloro-2,3,3-trifluorocyclobutanecarbonitrile. —A mixture of 10 g. of 2-chloro-2,3,3-trifluorocyclobutanecarbonitrile (I), b. p. 164°, prepared by heating chlorotrifluoroethylene, acrylonitrile and a polymerization inhibitor for eight hours at 150° and autogenous pressure according to the general procedure of Barrick,² was heated with 50 ml. of concd. hydrochloric acid under reflux on a steam-bath overnight. Two liquid layers, both miscible with sodium hydroxide solution, were present at the end of this time. After being taken up in alkali the combined solutions were reacidified, but only a small amount of acid-insoluble material separated. The mixture was extracted five times with 50-ml. portions of ether, and the combined extracts were dried over sodium sulfate. After evaporation of the ether about 4 g. of crystals, m. p. 85–94°, was obtained. Recrystallization from hot toluene gave 2 g. of the dibasic acid previously described, identified by its melting point alone and in admixture with the sample described previously.

A mixture of 10 g. of the 2-chloro-2,3,3-trifluorocyclobutanecarbonitrile (I) with 50 g. of 20% aqueous sodium hydroxide solution darkened immediately with the liberation of ammonia and with a temperature rise from 25° to vigorous reflux. A dark solid formed. After standing overnight, the alkaline solution was filtered to remove the solid and the filtrate acidified with hydrochloric acid. The dark acid solution was extracted with five 50-ml. portions of ether, the extract dried, and the solvent removed. From the residual dark oil upon recrystallization from toluene, the same dibasic acid, identified by melting point alone and in admixture with a known sample, was obtained in low yield.

3. Preparation of α,α -Difluoroglutaric Acid by Hydrolysis of 2,2,3,3-Tetrafluorocyclobutanecarbonitrile. —Alkaline hydrolysis of 2,2,3,3-tetrafluorocyclobutanecarbonitrile (II), prepared by the method described in the literature,¹ with an equal weight of 25% sodium hydroxide solution for eight hours at reflux gave an isolated yield of recrystallized dibasic acid of about 30%. The purified product melted at 103–105° alone or in admixture with the acid from 2-chloro-2,3,3-trifluorocyclobutanecarbonitrile

and showed agreement with the calculated values for fluorine content and neutral equivalent.

Anal. Calcd. for $C_5H_8F_2O_4$: F, 22.6; neut. equiv., 84.0. Found: F, 23.9, 24.1; neut. equiv., 84.5, 84.5.

The dimethyl ester, b. p. 65° (12 mm.), was prepared in 70% yield from the free acid and methanol with *p*-toluenesulfonic acid as a catalyst.⁴

Anal. Calcd. for $C_7H_{10}F_2O_4$: F, 19.4; sapon. equiv., 98. Found: F, 19.2, 19.0; sapon. equiv., 95.2, 96.6.

4. Preparation of *N*-Octyl α,α -Difluoroglutaramic Acid, Methyl Ester.⁴—A mixture of 20 g. of dimethyl difluoroglutarate, 14.2 g. of *n*-octylamine and 35 g. of toluene was heated for four hours with slow distillation of 3.8 g. of methanol and toluene. The vapor temperature rose from 63° to 79.5°. Further heating at reflux for 3.5 hours, after the addition of 0.5 g. of triethylamine hydrochloride, failed to produce any reduction in the distillation temperature. The reaction mixture was cooled, washed with water, dilute hydrochloric acid, dilute sodium bicarbonate solution and with water until neutral. After drying over sodium sulfate and removal of the solvent, the residual waxy solid was distilled at 172–180° (3.7 mm.). Twenty-five and eight-tenths grams of distillate, which crystallized to form shiny plates, m. p. 38–39.5°, was obtained. Analyses indicated the amic ester structure rather than the imide.

Anal. Calcd. for $C_{13}H_{21}F_2NO_2$ (imide): N, 5.33; mol. wt., 261. Calcd. for $C_{14}H_{23}F_2NO_3$ (amide ester): N, 4.77; mol. wt., 293. Found: N, 4.93, 4.90; mol. wt. (ebullioscopic in benzene), 289, 300.

Summary

A novel cleavage of a cyclobutane ring has been observed in the hydrolysis of tetrafluoro- and chlorotrifluorocyclobutanecarbonitriles to α,α -difluoroglutaric acid.

(4) We are indebted to Dr. N. E. Searle and Mr. H. E. Cuperly of this laboratory for the details of these experiments.

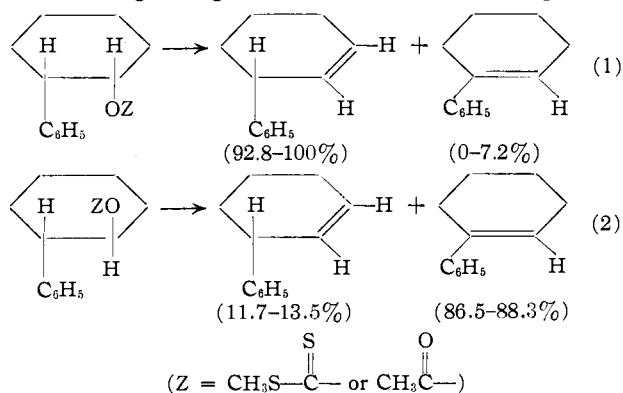
WILMINGTON, DELAWARE RECEIVED DECEMBER 19, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Studies on the Mechanism of Chugaev and Acetate Thermal Decompositions. II. *cis*- and *trans*-2-Methyl-1-tetralol

BY ELLIOT R. ALEXANDER AND ANTON MUDRAK¹

In an earlier communication² it was shown that during Chugaev^{3,4} and acetate⁵ decompositions of *cis*-2-phenylcyclohexanol lead predominantly to 3-phenylcyclohexene (Equation 1), whereas similar decompositions of the corresponding derivatives of the *trans*-alcohol lead principally to 1-phenylcyclohexene (Equation 2). This work supports the conclusion reached by other investigators³ that in contrast to most elimination reactions, which appear to involve elements *trans* to each other, the Chugaev reaction proceeds with the preferential elimination of a *cis* hydrogen atom. Furthermore, it supports the suggestion that transitory six-membered rings are formed



(Equation 3).

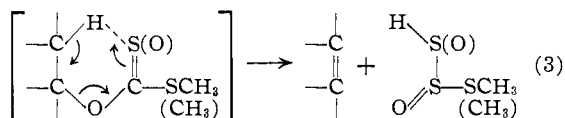
(1) Colgate-Palmolive-Peet Company, Jersey City, New Jersey.

(2) Alexander and Mudrak, *THIS JOURNAL*, **72**, 1810 (1950).

(3) Hüchel, Tappe and Legutke, *Ann.*, **543**, 191 (1940).

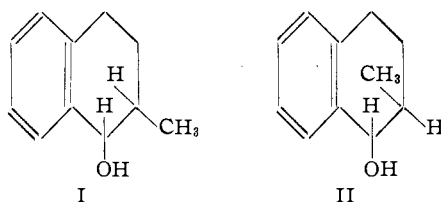
(4) Stevens and Richmond, *THIS JOURNAL*, **63**, 3132 (1941).

(5) Hurd and Blunck, *ibid.*, **60**, 2421 (1938).



In both of the studies which have been carried out,^{2,3} however, it was observed that in addition to the olefin to be expected of *cis*-elimination, some of the isomeric olefin was obtained (see, for example, Equations 1 and 2). An important aspect of the reaction mechanism, therefore, is the origin of the olefin apparently formed by *trans*-elimination. The question arises as to whether elimination involves two different processes occurring at different rates or whether the reaction proceeds by the exclusive removal of the *cis*- β -hydrogen atom, followed by rearrangement.

It was the object of this work to answer the question by studying Chugaev and acetate thermal decompositions of a cyclic alcohol having only one β -hydrogen atom either *cis* or *trans* to the hydroxyl group. In this paper is described the synthesis of *cis*(I)- and *trans*(II)-2-methyl-1-tetralol together with a study of the decomposition of the acetates and methyl xanthates of these alcohols.



Experimental⁶

α -Methyl- β -benzoylpropionic Acid.—This compound was prepared by a modification of the method of Krollpfeifer and Schäfer.⁷ To a suspension of 284 g. (2.13 moles) of anhydrous aluminum chloride in 450 ml. of dry, thiophene-free benzene was added a solution of 110 g. (0.97 mole) of methylsuccinic anhydride⁸ in 115 ml. of benzene at such a rate as to keep the mixture refluxing briskly. After all the anhydride had been added, the mixture was refluxed for thirty minutes on a steam-bath and the product was isolated according to the procedure of Somerville and Allen.⁹ The crude product (184 g.) was recrystallized twice from benzene to yield 110 g. (60%) of α -methyl- β -benzoylpropionic acid, m. p. 139–140.5°.

α -Methyl- γ -phenylbutyric Acid.—The reduction of α -methyl- β -benzoylpropionic acid was performed by the method of Horning and Reisner¹⁰ which, in our hands, gave better results than a Clemmensen reduction.¹¹ The keto-acid was reduced in three portions of 33 g. (0.17 mole), using 100 ml. of glacial acetic acid as a solvent and 3 g. of palladium chloride on carbon (5% Pd) as a catalyst.¹² With an initial pressure of 40–45 p. s. i. and a tem-

perature of 65° the reduction was complete in thirty to forty minutes. After removal of the catalyst and solvent, the combined products from the three reductions were distilled to yield 79 g. (85%) of α -methyl- γ -phenylbutyric acid, b. p. 125–135° (0.1–0.2 mm.),⁷ n_D^{20} 1.5115.

The *p*-phenylphenacyl ester of α -methyl- γ -phenylbutyric acid melted at 63–65° (from ethanol). Carter¹³ reported 62–63°.

2-Methyl-1-tetralone.—The ring-closure of α -methyl- γ -phenylbutyric acid was accomplished by the general procedure of Bachmann and Thomas.¹⁴ Thus, from 86 g. (0.48 mole) of the substituted butyric acid, 400 ml. of benzene, 108 g. (0.52 mole) of phosphorus pentachloride and a solution of 156 g. (0.6 mole) of stannic chloride in 200 ml. of benzene, was obtained 70.2 g. (92%) of 2-methyl-1-tetralone after distillation through an electrically-heated eight-inch column packed with glass helices; b. p. 79–80° (1 mm.); n_D^{20} 1.5447.¹⁶ The over-all yield of the product based on methylsuccinic anhydride was 47%.

The semicarbazone melted at 193–195°.¹⁶

Of a number of methods which were investigated for the preparation of 2-methyl-1-tetralone, another which was found to be equally satisfactory from the point of view of convenience and yield was one based on the preparation of 2-methyl-2-carbomethoxy-1-tetralone¹⁶ followed by hydrolysis of the keto-ester according to the procedure of Bachmann, Cole and Wilds.¹⁷ Several runs were carried on a scale of about 0.85 mole with an over-all yield of 43% based on 1-tetralone.

***trans*-2-Methyl-1-tetralol.**—The following procedure is typical of the many reductions which were carried out with various amounts of 2-methyl-1-tetralone.

Ten grams (0.0625 mole) of 2-methyl-1-tetralone dissolved in 150 ml. of 95% ethanol was reduced in the manner already described² with 10.0 g. (0.43 mole) of metallic sodium. Distillation of the product gave a forerun of 1.8 g. of low-boiling material and a main fraction (6.6 g.) boiling at 96–104° (0.4–0.5 mm.). On standing, this fraction partially solidified. Recrystallization from petroleum ether (42–50°) gave 2.0 g. of crude *trans*-2-methyl-1-tetralol melting at 60–65°. If the filtrate from this recrystallization was added to another batch of 2-methyl-1-tetralone being reduced, the yield of the *trans* alcohol was increased to 3–4 g. The combined products from several reductions were recrystallized an additional three or four times to a constant melting point of 74–75°.

Anal. Calcd. for C₁₁H₁₄O: C, 81.44; H, 8.70. Found: C, 81.61; H, 8.62.

More material was obtained from the mother liquors by evaporation of the solvent and conversion of the residue to a mixture of 3,5-dinitrobenzoates.¹⁸ Fractional crystallization from methanol or petroleum ether (90–120°) gave the less soluble 3,5-dinitrobenzoate of *trans*-2-methyl-1-tetralol as stout, light-yellow needles, m. p. 155–156°.

Anal. Calcd. for C₁₃H₁₆N₂O₆: N, 7.86. Found: N, 7.75.

Saponification of this derivative was carried out as follows: Five grams (0.014 mole) of the 3,5-dinitrobenzoate was heated for one hour at 160° with 60 ml. of 6% potassium hydroxide in diethylene glycol. The product was then steam-distilled from the reaction mixture and after cooling the distillate in an ice-bath, 1.4 g. (61% from the 3,5-dinitrobenzoate) of *trans*-2-methyl-1-tetralol, m. p. 72–74°, was collected on a filter.

(6) All melting points and boiling points are uncorrected.

(7) Krollpfeifer and Schäfer, *Ber.*, **56**, 631 (1923).

(8) Prepared in 85% yield from methylsuccinic acid by the method of Fieser and Martin, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 560.

(9) Somerville and Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 81.

(10) Horning and Reisner, *THIS JOURNAL*, **71**, 1036 (1949).

(11) Fieser, *et al.*, *ibid.*, **70**, 3203 (1948).

(12) Mozingo, "Organic Syntheses," Vol. 26, John Wiley and Sons, Inc., New York, 1946, p. 77.

(13) Carter, *THIS JOURNAL*, **62**, 2244 (1940).

(14) Bachmann and Thomas, *ibid.*, **64**, 95 (1942).

(15) English and Cavaglieri *ibid.*, **65**, 1085 (1943) reported n_D^{20} 1.5585 and Krollpfeifer and Schäfer⁷ reported n_D^{20} 1.5515 for 2-methyl-1-tetralone.

(16) Bachmann and Thomas, *ibid.*, **63**, 599 (1941).

(17) Bachmann, Cole and Wilds, *ibid.*, **62**, 824 (1940).

(18) Fuson and Shriner, "Identification of Organic Compounds," third edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 164.

cis-2-Methyl-1-tetralol.—A solution of 10 g. (0.0625 mole) of 2-methyl-1-tetralone in 40 ml. of absolute ethanol was hydrogenated at room temperature and a pressure of 45 p. s. i., using 4 g. of Raney nickel as catalyst. The theoretical amount of hydrogen was absorbed in about nine hours. After removing the catalyst by filtration, the ethanol was evaporated under reduced pressure. In the final stages of the evaporation an oil pump was used to remove the last traces of solvent. The residue was then mixed with 10 g. (0.084 mole) of phenyl isocyanate and allowed to stand for several hours. The solid reaction product was broken up, transferred to a Büchner funnel, and washed with cold petroleum ether. The yield of crude product, m. p. 110–115°, was 15.1 g. After four recrystallizations from petroleum ether (96–101°) there remained 11.8 g. (67% based on 2-methyl-1-tetralone) of the phenylurethan melting at 122–124°.

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 76.62; H, 6.69.

In order to regenerate the purified *cis* alcohol, 60 ml. of 6% potassium hydroxide in diethylene glycol and 11.8 g. of the phenylurethan were heated at 150–160° for one hour. The reaction mixture was then steam-distilled, the distillate acidified with hydrochloric acid, and the product extracted with four 30-ml. portions of ether. The combined ether extracts were washed once with dilute sodium carbonate solution, once with water, dried over anhydrous magnesium sulfate and distilled. The yield of purified *cis*-2-methyl-1-tetralol, b. p. 90–94° (0.2–0.3 mm.); n_D^{20} 1.5502, was 6.1 g. (90% from the phenylurethan).

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.34; H, 8.82.

Methyl *trans*-2-Methyl-1-tetralylxanthate.—This material was prepared by the method previously described.² From 1.9 g. (0.012 mole) of *trans*-2-methyl-1-tetralol was obtained 2.4 g. (81%) of the xanthate melting at 58–59°.

Anal. Calcd. for $C_{13}H_{16}OS_2$: C, 61.86; H, 6.39. Found: C, 62.09; H, 6.59.

***trans*-2-Methyl-1-tetralyl Acetate.**—Seven grams (0.043 mole) of the *trans* alcohol was converted to the acetate by the acetyl chloride-pyridine method² in 96% yield. The acetate was recrystallized twice from 85% ethanol to give an analytical sample melting at 61–62°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.37; H, 8.08.

Methyl *cis*-2-Methyl-1-tetralylxanthate.—This xanthate, prepared by the usual procedure² could not be induced to crystallize. However, purification was accomplished by distillation from a short-path distilling flask under reduced pressure. The distillate (bath temperature 160°, 0.06 mm.) was collected in a number of small fractions, one of which solidified on standing. With the seed thus obtained, crystallization was induced in other fractions. Approximately 0.8 g. (17%) of the xanthate, m. p. 68–70°, was obtained from 3 g. (0.018 mole) of *cis*-2-methyl-1-tetralol. Three recrystallizations from absolute ethanol gave a pure white product melting at 71–72°.

Anal. Calcd. for $C_{13}H_{16}OS_2$: C, 61.86; H, 6.39. Found: C, 61.84; H, 6.47.

***cis*-2-Methyl-1-tetralyl Acetate.**—This acetate was prepared by the usual method² in 95% yield; b. p. 86–92° (0.2–0.3 mm.); n_D^{20} 1.5192.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.70; H, 8.01.

2-Methyl-3,4-dihydronaphthalene.—During one of the exploratory runs, a sample of 2-methyl-1-tetralone was reduced with copper-chromium oxide at 100° and a pressure of 1600 p. s. i. Distillation gave a hydrocarbon, b. p. 63–65° (0.6 mm.), n_D^{20} 1.5751, d_4^{20} 0.9837, which decolorized potassium permanganate solution and readily absorbed bromine in carbon tetrachloride. Apparently dehydration occurred during the distillation to give 2-methyl-3,4-dihydronaphthalene.

Anal. Calcd. for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.45; H, 8.29.

The 2-methyl-3,4-dihydronaphthalene formed a picrate, m. p. 70–74°, which, because of its instability, could not be purified for analysis. It was, however, found useful as a derivative for identifying the products formed in the decomposition of the xanthates and acetates.

Decomposition of the Xanthates.—The apparatus used for the decomposition of the xanthates consisted of a pear-shaped flask of about 15-ml. capacity connected in series with a condenser, a safety bottle, a bubbler, a gas-buret and a leveling-bulb. The last three units were filled to convenient levels with a 50% solution of sulfuric acid. A 400-ml. beaker filled with paraffin oil and heated by a "Glas-Col" beaker mantle served as an oil-bath. The bath was arranged in such a manner that it could be raised easily so as to immerse completely the flask containing the xanthate. The bath was provided with a stirrer to insure uniform heating. A blank was run to determine the amount of expansion of the air in the flask when it was immersed in the oil-bath at 100°. It was found that the temperature of the bath fell from 100 to 98° when the flask was immersed in the oil. Consequently the results are given for the range 98–100°.

One-half gram (0.002 mole) of xanthate was placed in the flask, the initial buret reading was taken, and the oil-bath (at 100°) was quickly raised into position. The combined value of the carbonyl sulfide and methyl mercaptan was read at regular intervals until the evolution of gases began to slacken. After correcting for the blank, the per cent. decomposition, as measured by the volume of gases evolved, was plotted against time (Fig. 1).

The product which was formed from the decomposition of the *trans*-xanthate had a refractive index of 1.5741 (20°) and formed a picrate which melted at 66–69°. A mixed melting point with an authentic sample of 2-methyl-3,4-dihydronaphthalene picrate showed no depression.

The *cis* xanthate did not decompose at 98–100°. The original xanthate was recovered unchanged at the conclusion of the experiment.

Pyrolysis of the Acetates.—The apparatus used for the pyrolysis of the acetates was described in a previous article.² The pyrolysis tube was heated to the desired temperature and the receiver was immersed in an ice-bath. One ml. of the acetate was introduced into a dropping funnel and allowed to drop at the rate of one drop every two seconds into the tube. As soon as all the acetate had been introduced, the dropping funnel was rinsed with 10 ml. of purified dioxane, which was then allowed to drop into the tube at a rate of about one drop per second.

The pyrolysate was diluted with about 50 ml. of water and was titrated with 0.1 *N* sodium hydroxide, using phenolphthalein as an indicator. The same procedure was used for blank runs at each temperature, with dioxane alone. The titers obtained in the blank runs were subtracted from those of the pyrolyzed acetate samples at the corresponding temperature. In Fig. 2 the volume of 0.1 *N* sodium hydroxide employed is plotted against the temperature. The per cent. decomposition to which this corresponds is also shown.

The product obtained from the pyrolysis of the *trans*-acetate formed a picrate which melted at 67–71°. A mixed melting point of this material with 2-methyl-3,4-dihydronaphthalene picrate showed no depression.

Because decomposition of the *cis*-acetate was only partially complete at 550°, a second pyrolysis was carried out at 650° in order to obtain enough product for characterization. The product, n_D^{20} 1.5820, formed a picrate melting at 114–115°. No depression of the melting point was noted when this picrate was mixed with the picrate of an authentic sample of 2-methylnaphthalene.¹⁹

Attempted Dehydrogenation of 2-Methyl-3,4-dihydronaphthalene.—Four grams of 2-methyl-3,4-dihydronaphthalene and 1.65 g. of glacial acetic acid were passed through the pyrolysis tube at 650°. The product was washed with 5% sodium hydroxide and water, dried over anhydrous magnesium sulfate and distilled. The index

of refraction of the product was the same as that of the original 2-methyl-3,4-dihydronaphthalene, indicating that the hydrocarbon had undergone no change.

Results and Discussion

Synthesis of *cis*- and *trans*-2-Methyl-1-tetralol.—The preparation of *cis*- and *trans*-2-methyl-1-tetralol was carried out by the reduction of 2-methyl-1-tetralone. In spite of a careful study of different methods and conditions, considerable difficulty was encountered in the isolation of pure isomers. The *trans* isomer, being a solid, was the more readily accessible of the two. It was obtained by repeated recrystallization of the mixture of products resulting from the reduction of 2-methyl-1-tetralone with sodium and alcohol. Additional material could be recovered from the recrystallization mother liquors, by evaporation of the solvent and treatment of the residue with 3,5-dinitrobenzoyl chloride. *trans*-2-Methyl-1-tetralyl 3,5-dinitrobenzoate could be fractionally crystallized from the mixture and saponification gave the *trans*-alcohol in good purity.

The *cis*-alcohol was found to be a liquid at room temperature and we were, therefore, particularly anxious to find a solid derivative suitable for purification. Investigation revealed a curious but extremely fortunate circumstance: *The alcohol prepared from the room temperature hydrogenation of 2-methyl-1-tetralone with Raney nickel formed a phenylurethan. The alcohol prepared by a sodium reduction did not.* When this fact was learned, the liquid isomer, which we believe to be the *cis*-alcohol, was readily obtained in pure form by saponification of the phenylurethan which had been recrystallized to constant melting point.

With neither of these isomers has the stereochemistry been unequivocally determined. The structures have been assigned on the basis of the manner in which they have been synthesized²⁰ and the behavior of the xanthates on heating.^{2,3}

Thermal Decomposition.—In Fig. 1 is shown a plot of per cent. decomposition (as measured by the gases evolved) against time for the methyl xanthates of *cis*- and *trans*-2-methyl-1-tetralol. It is evident that while the *cis*-isomer is stable at 98–100°, methyl *trans*-methyl-1-tetralylxanthate is rapidly decomposed. By a mixed melting point determination of its picrate, the hydrocarbon formed was shown to be 2-methyl-3,4-dihydronaphthalene.

In Fig. 2 is shown the per cent. decomposition of the *cis*- and *trans*-acetates when they were passed at various temperatures through an electrically heated tube packed with glass beads. Here, too, it can be seen that the *cis*-isomer is much more stable than the *trans*. It is interesting, however, that while the *trans*-isomer led to 2-methyl-3,4-dihydronaphthalene, decomposition of the *cis*-isomer at 650° gave 2-methylnaphthalene. De-

(20) Skita, *Ber.*, **53**, 1792 (1920); *Ann.*, **427**, 256 (1922); Vavon and Anziani, *Bull. soc. chim.*, **41**, 1638 (1927).

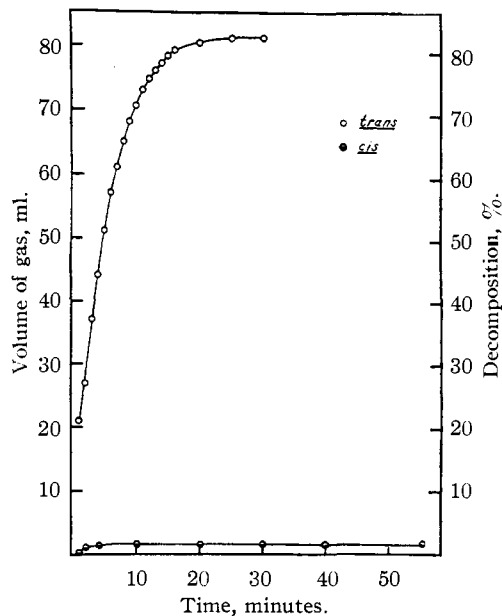


Fig. 1.—Decomposition of the xanthates of *cis*- and *trans*-2-methyl-1-tetralol at 98–100°: O, *trans*; ●, *cis*.

hydrogenation appears to have occurred during the thermal decomposition of the acetate, since treatment of 2-methyl-3,4-dihydronaphthalene under the same conditions produced no dehydrogenation.

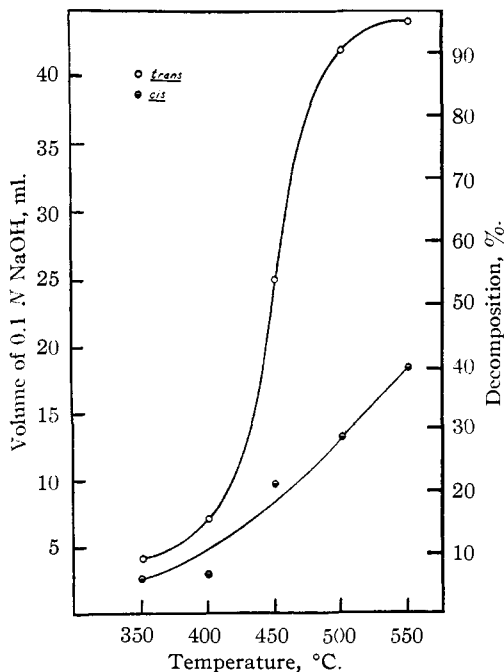


Fig. 2.—Pyrolysis of the acetates of *cis*- and *trans*-2-methyl-1-tetralol: O, *trans*; ●, *cis*.

It is tempting to conclude from this work that Chugaev thermal decompositions involve only *cis*-hydrogen atoms and that simple dehydration

by the pyrolysis of an acetate may also. There is one feature concerning xanthates, however, which prevents such a conclusion. It has been reported^{21,22} that some xanthates are converted to a "stable form" if they are distilled. Such "stable forms" are not the dithiocarbonates but they have the same composition, molecular weight and melting point as the xanthate from which they are derived. The *cis*-xanthate, it will be observed, had to be distilled in order to obtain a pure sample. We have no evidence of it, but if such a "stable form" resulted from the distillation of the *cis*-compound, data such as those shown in Fig. 1 might be obtained.

Concerning pyrolysis of the acetates, it is certainly clear that the *cis*-form is more stable than the *trans*-form. The fact that 2-methylnaphthalene, rather than 2-methyl-3,4-dihydronaphthalene, was isolated, however, may indicate that the acetic acid measured in the pyrolysis of the *cis*-acetate was formed by another path of reaction.

(21) McAlpine, *J. Chem. Soc.*, 1114 (1931); 906 (1932).

(22) Bulmer and Mann, *ibid.*, 666 (1945).

Acknowledgment.—We are indebted to Miss Rachel Kopel and Miss Emily Davis for the microanalyses reported in this paper.

Summary

Two isomers of 2-methyl-1-tetralol have been synthesized. One of these, which we believe to be the *trans*-isomer, was prepared by a sodium-ethanol reduction of 2-methyl-1-tetralone. The other, which we believe to be the *cis*-isomer, was prepared by hydrogenation of the same ketone in the presence of Raney nickel.

The thermal decomposition of *trans*-2-methyl-1-tetralyl acetate and methyl-*trans*-2-methyl-1-tetralylxanthate proceeds at considerably lower temperatures than does the decomposition of the corresponding *cis*-isomers. These results are in agreement with the point of view that the Chugaev reaction and the simple thermal decomposition of acetates involve the intermediate formation of a transitory six-membered ring with a *cis*- β -hydrogen atom.

URBANA, ILLINOIS

RECEIVED DECEMBER 17, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XI. Cuprous Chloride Catalyzed Hydrolysis of Several Allylic Chlorides¹

BY LEWIS F. HATCH, ALLEN N. BROWN AND HOWARD P. BAILEY

There have appeared in the literature several references^{2,3,4} to the cuprous chloride catalyzed hydrolysis of allylic chlorides. The present paper presents an extension of these studies to include a number of compounds not heretofore investigated. From these data it has been possible to elucidate the influence on this reaction of certain substituents on both the number one and number two carbon atoms of allyl chloride and to assign geometrical configuration to the two isomers of 1,3-dichloro-2-methylpropene.

Experimental

Cuprous Oxide.—Baker C. P. Analyzed (98.8%) cuprous oxide was used without further purification.

Hydrochloric Acid.—The 1.5% hydrochloric acid used in this investigation was prepared by diluting 33 ml. of Reagent Grade concentrated hydrochloric acid to one liter with distilled water.

All other inorganic reagents were of Reagent Grade or its equivalent.

The following compounds were furnished for this investigation by Shell Chemical Co., San Francisco, California, and in each case the compound was distilled through a

four-foot, glass-helix packed vacuum jacketed column before use.

Allyl Chloride.—Boiling point 44.4° (744 mm.).

Methallyl Chloride.—Boiling point 72.1° (742 mm.).

2,3-Dichloro-1-propene.—Boiling point 93.4° (746 mm.).

cis- and *trans*-1,3-Dichloropropene.—These isomers were separated using a Podbielniak Hypercal distillation column, then redistilled through a two-foot glass-helix packed column immediately before use.

cis-1,3-Dichloropropene.—Boiling point 104° (746 mm.); n_D^{25} 1.4650 (lit.⁵ n_D^{25} 1.4652).

trans-1,3-Dichloropropene.—Boiling point 112° (745 mm.); n_D^{25} 1.4712 (lit.⁵ n_D^{25} 1.4712).

2-Bromo-3-chloro-1-propene.—The 2-bromo-3-chloro-1-propene (Halogen Chemicals, Columbia, South Carolina) was distilled at a pressure of 50 mm. through a two-foot glass-helix packed column. The fraction used boiled at 45.7°; n_D^{25} 1.4968 (lit.⁶ n_D^{25} 1.4968). This compound was not stable and it was necessary to use it immediately after fractionation.

1,1,3-Trichloro-2-methyl-1-propene.—This trichloride (Halogen and Perfume Chemicals, Columbia, South Carolina) was distilled at 36 mm. pressure through a two-foot glass-helix packed column. The fraction used boiled at 71.5°; n_D^{25} 1.4932 (lit.⁶ n_D^{25} 1.4933).

α and β -1,3-Dichloro-2-methylpropene.—The isomeric 1,3-dichloro-2-methylpropenes were prepared from methallyl chloride⁷ which was chlorinated to 1,2,3-trichloro-2-methylpropane using sulfuryl chloride. The trichloride was dehydrochlorinated to a mixture of the 3-chloro-2-methyl-2-propen-1-ols which was separated by means of a

(5) Hatch and Perry, *ibid.*, 71, 3262 (1949).

(6) Hatch, Gordon and Russ, *ibid.*, 70, 1093 (1948).

(7) Hatch, Russ and Gordon, *ibid.*, 69, 2614 (1947).

(1) Presented in part at the Southwest Regional Meeting of the American Chemical Society, Shreveport, La., December 11, 1948.

(2) Williams, *Trans. Am. Inst. Chem. Engs.*, 37, 157 (1941).

(3) Williams, *Chem. Met. Eng.*, 47, 834 (1940).

(4) (a) Hatch and Estes, *THIS JOURNAL*, 67, 1730 (1945); (b) Hatch and Roberts, *ibid.*, 68, 1196 (1946); (c) Hatch and Ballin, *ibid.*, 71, 1041 (1949); (d) Hatch and Gerhardt, *ibid.*, 71, 1679 (1949).