acid. After an 8-hr. period no oil remained, and the solution was filtered hot to remove suspended particles of carbon, treated with Norit and evaporated to dryness *in vacuo.* The residual solid was thoroughly extracted with 250 ml. of ether, the ether extract dried over anhydrous magnesium sulfate, again treated with Norit, concentrated to about 100 ml., and hexane added till slight clouding was observed. On cooling the solution a white crystalline solid separated, m.p. 120–125°; on admixture with a sample of V from hydrolysis of II, m.p. 122–127°.

The crude *4,4-dinitro-2-hydroxyheptanedioic acid* was recrystallized from acetonitrile–heptane–benzene to yield a slightly higher melting sample, m.p. 128–131°; and again from ethyl acetate–benzene to give a sample melting at 128.8–134.4°. The latter, on admixture with the sample of V from hydrolysis of II, melted from 129.5 to 138°.

Anal. Calcd. for $C_7H_{10}N_2O_9$: C, 31.60; H, 3.79; N, 10.54. Found: C, 31.99, 32.04; H, 3.79, 3.85; N, 10.09, 9.80.

Evidently the sample of V prepared in this way was contaminated by a small amount of impurity which could not readily be removed by crystallization. Infrared spectra of both samples of V were superimposable and x-ray diffraction patterns confirmed that they were indeed identical.

Acknowledgment. We are grateful to Dr. J. R. Holden and Mr. H. T. Simmons for determining molecular weights by the x-ray method and to Messrs. F. Taylor, Jr., and B. Wilkerson for supplying some of the intermediates. Drs. J. C. Dacons, O. H. Johnson, and D. V. Sickman contributed helpful suggestions.

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Directive Influences in Olefin Formation

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Received September 25, 1961

In the formation of olefin mixtures by elimination reactions of 3-heptyl derivatives, bimolecular processes (chloride plus base, quaternary ammonium hydroxide plus heat, or alcohol with sulfuric or phosphoric acid) give 55–66% of 2-heptene and 45–34% of 3-heptene, but monomolecular processes (pyrolysis of hydrogen phthalate, xanthate, or amine oxide, and probably aluminum oxide dehydration) give 43–48% of 2-heptene and 57–52% of 3-heptene. These results are most easily explained by electronic effects in the first group, and by steric effects in the second group. Dehydration of 2,4-dimethyl-3-hexanol with sulfuric or phosphoric acid gives 58–60% of 2,4-dimethyl-2-hexene and 42–40% of the 3-hexene, which is in accord with the results of the 3-heptyl series, but the bromide and base give only 51% of the 2-hexene: pyrolyses of the acetate and hydrogen phthalate give high (100 and 75%) proportions of the 2-hexene, but aluminum oxide yields only 49%. Pyrolysis of 2,5-dimethyl-3-hexyl acetate gives 68% of 2,5-dimethyl-3-hexene.

The formation of olefins by elimination reactions is a synthetic process of long standing, but more than one product is usually observed. The pyrolytic cis eliminations have been covered in a recent review[2] dealing with esters, xanthates, amine oxides, and other starting materials. Other elimination reactions such as the action of strong acids on alcohols, bases on halides, and pyrolysis of quaternary ammonium hydroxides have been the basis of the formulation of the Hofmann[3] and Saytzeff[4] rules. Despite the prolonged attention granted such reactions it cannot be said that all factors are well understood.[5]

In this paper eliminations have been studied in which, for the most part, there is no obvious difference in predictions based on either Hofmann or Saytzeff rules. This would apply either to the 3-heptyl or to the 2,4-dimethyl-3-hexyl derivatives, but in the case of the pyrolysis of 2,5-dimethyl-3-hexyl acetate there was potential steric hindrance so located that the normally favored elimination might yield the minor quantity of product.

Dehydration of 3-heptanol with sulfuric acid gave an olefin mixture in which the 2-heptene:3-heptene ratio was 60.4:39.6. Dehydration of the 3-heptanol with phosphoric acid gave the product ratio 55.0:45.0. Refluxing 3-chloroheptane with methanolic potassium hydroxide gave 62.8:37.2. Heating 3-heptyltrimethylammonium hydroxide gave 65.8:34.2. These are all reactions best interpreted as proceeding by concerted mechanisms, and the favored product in each case is 2-heptene. This should be the more stable isomer on the basis of hyperconjugation, although no difference in stability is apparent in available data.[6]

Pyrolysis of 3-heptyl methyl xanthate gave an olefin mixture in which the 2-heptene:3-heptene ratio was 46.7:53.3. 3-Heptyldimethylamine oxide gave a ratio of 44.8:55.2. 3-Heptanol over alumina gave 47.5:52.5 and pyrolysis of 3-heptyl hydrogen phthalate gave 42.6:57.4. These reactions all involve a cyclic intramolecular transition state if one can assume that the 3-heptanol-alumina dehydra-

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[1] Du Pont Fellow, 1957–58.

[2] C. H. DePuy and R. W. King, *Chem. Revs.*, 60, 431 (1960).

[3] A. W. Hofmann, *Ann.*, 79, 11 (1851).

[4] A. Saytzeff, *Ann.*, 179, 296 (1875).

[5] See, for example, E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, New York, 1959, p. 472.

[6] R. R. Dreisbach, *Physical Properties of Chemical Compounds—II* (Number 22 of the Advances in Chemistry Series), American Chemical Society, Washington, D. C., (1959), p. 247–250.

tion involves some sort of heptanol oxygen to aluminum complex, with an alumina oxygen attacking a β-hydrogen. In the case of the phthalate pyrolysis, the heptenes were resolved into four fractions. It is known that *trans*-2-heptene is lower boiling than the *cis* isomer[7] and should be the earlier of the 2-heptene peaks; if it is assumed that the *trans*-3-heptene precedes the *cis*, the proportions of the four olefins are: *trans*-3-heptene, 37.6%; *cis*-3-heptene, 19.9%; *trans*-2-heptene, 30.0%; and *cis*-2-heptene, 12.5%. These results agree well with those obtained in the pyrolysis of 3-heptyl acetate.[8] The predominance of 3-heptene seems to indicate that methyl-butyl repulsion in the transition state is greater than ethyl-propyl. In either case, repulsion is less in the transition state leading to the *trans* form.[9]

Eliminations from 2,4-dimethyl-3-hexyl derivatives do not group so conveniently into two classes. Dehydration of 2,4-dimethyl-3-hexanol with sulfuric acid gives 60.2% of the 2-hexene and 39.8% of the 3-hexene; with phosphoric acid the proportion is 58.3% and 41.7%. Refluxing 3-bromo-2,4-dimethylhexane with methanolic potassium hydroxide gives 50.7% of the 2-hexene and 49.3% of the 3-hexene, a poor agreement with the dehydrations and with the 3-heptyl series. Dehydration of 2,4-dimethyl-3-hexanol over alumina gives 48.8% and 51.25% of 2- and 3-hexene. Pyrolysis of 2,4-dimethyl-3-hexyl hydrogen phthalate gives 74.6% and 25.4%, but pyrolysis of the acetate gives nearly all 2,4-dimethyl-2-hexene: the first run gave 0.5% of the 3-hexene, but a repetition with the quartz thermometer removed (as a suspected cause of possible rearrangement) showed no detectable 2,4-dimethyl-3-hexene. The poor correlation between product mixtures and reaction types may well result from variable composition of the 2,4-dimethyl-3-hexyl diastereoisomers.

In an attempt to accentuate steric factors, 2,5-dimethyl-3-hexyl acetate was pyrolyzed. Gas chromatographic analysis showed the product to be 68% *sym*-diisopropylethylene. Comparing this with the pyrolysis of 2-methyl-3-hexyl acetate, which gives 27% of 2-methyl-2-hexene by loss of the tertiary hydrogen,[9] it is seen that blocking of the hydrogen on the fourth carbon by the 5-methyl results in slightly more reaction of the tertiary hydrogen. Turning to a consideration of the cyclic transition state, it appears that repulsion of an isobutyl for two methyls (loss of tertiary hydrogen) is greater than two isopropyls for each other (probably *trans*).

EXPERIMENTAL[10]

3-Heptanol. Matheson, Coleman, and Bell 3-heptanol was distilled through an 18-in. column packed with Raschig rings. The fraction boiling at 152° was used.

2,4-Dimethyl-3-hexanol and *2,5-dimethyl-3-hexanol.* The former was prepared by adding isobutyraldehyde to *sec*-butylmagnesium bromide in ether; the product, boiling in the range 156–158°, was obtained in 27% yield. The latter was prepared by adding isobutyraldehyde to isobutylmagnesium bromide; 31% yield of product boiling in the range 156–157°.

Dehydration of alcohols with phosphoric acid. A micro-distillation apparatus with a 50-ml. flask and Claisen head fitted with thermometer and dropping funnel was charged with 8.0 ml. of 85% phosphoric acid, heated to 155°, then 0.1 mole of the alcohol added over a period of 1 hr. The crude distillate was washed with 10% sodium hydroxide, then with water, then dried and distilled. In this and all subsequent collections of olefin mixtures destined for vapor chromatography the broadest possible fractions were collected to minimize losses of any of the isomeric products.

Dehydration of alcohols with sulfuric acid. A micro-distillation apparatus was charged with 0.1 mole of the alcohol and 10 ml. of 60% sulfuric acid. The mixture was heated until distillation ceased, then the crude product was washed, dried, and distilled.

Dehydration of alcohols over alumina. Under a nitrogen atmosphere, the alcohol was passed at a rate of 0.2 mole per hour through an inclined Pyrex tube packed with 6–8 mesh Alcoa activated alumina for a 25 cm. length and heated to 425°. The collected product was dried over calcium chloride and distilled.

3-Chloroheptane. 3-Heptanol was treated with pyridine and excess thionyl chloride. The upper layer was separated, washed, dried, and distilled, giving a 37% yield of 3-chloroheptane boiling at 145–146°.

3-Bromo-2,4-dimethylhexane. 2,4-Dimethyl-3-hexanol was treated at 5° or lower with phosphorus tribromide, then allowed to warm to room temperature overnight. The reaction mixture was poured into water, separated, and the organic layer washed, dried, and distilled, giving a 64% yield of the bromide boiling at 76–78° at 37 mm. pressure.

Dehydrohalogenation with base. One-tenth mole of the halide was refluxed for 20 hr. with a solution of 20 g. of potassium hydroxide in 40 ml. of methanol. The cooled mixture was poured into 160 ml. of cold water, and the organic layer was separated, washed, dried, and distilled.

Preparation of 2,4-dimethyl-3-hexyl acetate. One-tenth mole of 2,4-dimethyl-3-hexanol was cooled to 0°, then 7.8 g. of acetyl chloride was added slowly over a period of 30 min. The mixture was allowed to warm to room temperature, then washed, dried, and distilled. A 64% yield of 2,4-dimethyl-3-hexyl acetate was obtained; boiling range, 174–176°, n_D^{20} 1.4188.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.8; H, 11.6. Found: C, 70.1; H, 10.3.

Preparation of 2,5-dimethyl-3-hexyl acetate. The same procedure as above was used, giving a 62% yield of 2,5-dimethyl-3-hexyl acetate; boiling range, 174–176°, n_D^{20} 1.4132.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.8; H, 11.6. Found: C, 69.7; H, 11.9.

Preparation of alkyl hydrogen phthalates. Equimolar quantities of the alcohol and phthalic anhydride were heated under reflux for several hours. The crude product was dissolved in 10% sodium bicarbonate solution, washed with ether, acidified, filtered and dried, and recrystallized from petroleum ether. 3-Heptyl hydrogen phthalate was obtained in 46% yield, m.p. 53.5–54.5°. The 2,4-dimethyl-3-hexyl hydrogen phthalate is a new compound; it was obtained in 36% yield, m.p. 106–108°.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.1; H, 7.55. Found: C, 68.5; H, 7.67.

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(7) G. Egloff, *Physical Constants of Hydrocarbons*, Reinhold, New York (1939).

(8) E. E. Royals, *J. Org. Chem.*, **23**, 1822 (1958).

(9) D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

(10) Microanalyses by Drs. Weiler and Strauss, Oxford, England.

Preparation of S-methyl O-3-heptyl xanthate. Two-tenths mole of 3-heptanol was added to 0.2 g.-atom of sodium in 150 ml. of dry *p*-xylene and the mixture was stirred and refluxed for 3 hr. The mixture was cooled, then 150 ml. of dry ether and 30.5 g. of carbon disulfide was added and refluxed for 2 hr. Then 57 g. of methyl iodide was added and the mixture refluxed for twelve more hours. The mixture was cooled, filtered, low boiling material taken off below 80° at 20 mm., then a 52% yield of the product was collected at 105° at 5 mm.; n^{20}_{D} 1.5103.

Anal. Calcd. for $C_9H_{18}OS_2$: S, 31.1. Found: S, 28.3.

Decomposition of the esters. The acetates were passed through a 25-cm. heated zone (450–520°) with a slow stream of nitrogen. The collected material was washed with 5% sodium bicarbonate and water, then dried and distilled. The alkyl hydrogen phthalates were distilled in a micro-distillation apparatus under partial reflux until the vapor temperature reached 200°; the distillate was washed, dried, and distilled. The xanthate was heated in the same apparatus until distillation ceased; the distillate was washed with 20% sodium hydroxide, then twice with sodium plumbite, and finally water, then dried and distilled.

3-Dimethylaminoheptane. A mixture of 3-heptanone, dimethylamine, and platinum oxide in ethanol was loaded into an Aminco high pressure reaction vessel under 1100 p.s.i. of hydrogen, then heated to 260° and allowed to cool slowly overnight. Low boiling material was removed, then the desired amine was taken up in dilute hydrochloric acid, washed with ether, then liberated with sodium hydroxide. A 22% yield of 3-dimethylaminoheptane was obtained, boiling at 159–160°, n^{20}_{D} 1.4225. Neutral equivalent, calcd. for $C_9H_{21}N$, 143, Found: 143.

Preparation and pyrolysis of dimethyl-3-heptylamine oxide. 3-Dimethylaminoheptane was stirred for 30 hr. with an excess of 24% hydrogen peroxide, then another equivalent was added and the mixture heated to just below boiling for 40 min. The mixture was cooled and the excess hydrogen peroxide was destroyed with beef liver catalase. The mixture was filtered and the water removed under aspirator pressure. The residue was subjected to 2 mm. pressure and heated until decomposition of the amine oxide was complete. The distillate was washed with 10% hydrochloric acid, then with 10% sodium hydroxide, then with water, dried, and distilled.

Trimethyl-3-hepthylammonium iodide. 3-Dimethylaminoheptane in benzene was refluxed with an excess of methyl iodide for 20 min., then cooled and filtered. A 95% yield of the salt, melting 182–184°, was obtained.

Anal. Calcd. for $C_{10}H_{24}NI$: I, 44.5. Found: I, 42.5.

Preparation and pyrolysis of trimethyl-3-heptylammonium hydroxide. The iodide was dissolved in water, then shaken with silver oxide for 2 hr. The filtrate was transferred to a micro-distillation apparatus, and the water distilled; decomposition began as the rate of heating was increased and continued until no more distillate was collected. The distillate was washed with 5% hydrochloric acid, then with water, then dried and distilled.

Analysis of olefin mixtures. Olefin mixtures were analyzed by gas chromatography using a column of 6 ft. of benzyl ether and 6 ft. of *o*-nitrophenyl ether on firebrick. Reference samples were a commercial 2-heptene, 3-heptene from the pyrolysis of 4-heptyl hydrogen phthalate, and 2,4-dimethyl-2-hexene from dehydration of 2,4-dimethyl-2-hexanol with phosphoric acid. The heptenes were resolved into four distinct peaks, apparently in order of boiling point. The product of reaction of 2,4-dimethyl-3-chlorohexane with base was a mixture of only the two isomeric olefins expected, and was used to identify 2,4-dimethyl-3-hexene. The analysis of the 2,5-dimethylhexenes was performed on a column of 8 ft. of benzyl ether on firebrick at a later date, after a separation according to boiling point had been demonstrated for olefins on the column. Three peaks, corresponding to *cis*- and *trans*-diisopropylethylene and 2,5-dimethyl-2-hexene were obtained.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION, PITTSBURGH PLATE GLASS COMPANY]

Reaction of Cyclopentadiene with Hemiacetal Chlorides

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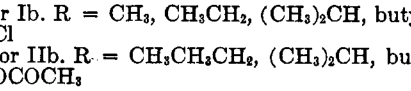
Received September 11, 1961

Cyclopentadiene reacts with hemiacetal chlorides to give alkoxymethyl-3-chlorocyclopentenes (I). Various transformations of I are described.

The reaction of olefins with hemiacetal chlorides which, in the simplest case, may be exemplified by the reaction of ethylene with chloromethyl ether,[1a] is well known in the literature.[1] Such reactions of cyclopentadiene, however, are unknown, except for one instance of its reaction with α-methoxybenzyl chloride reported by Straus and Thiel.[1c] It has now been shown that cyclopentadiene reacts smoothly with hemiacetal chlorides in the presence of tin tetrachloride to give chloro compounds I which are believed to be composed of either 5-alkoxymethyl-3-chlorocyclopentenes (Ia) or 4-alkoxymethyl-3-chlorocyclopentenes (Ib), or both. The chlorides I are unstable and, in the course of hours at room temperature or days in the cold, evolve hydrogen chloride and become discolored. Acids seem to accelerate the decomposi-

$$CH_2{=}CH_2 + ClCH_2OCH_3 \longrightarrow CH_3OCH_2CH_2CH_2Cl$$



Ia and/or Ib. R = CH_3, CH_3CH_2, $(CH_3)_2CH$, butyl, allyl; X = Cl

IIa and/or IIb. R = $CH_3CH_3CH_2$, $(CH_3)_2CH$, butyl, allyl; X = $OCOCH_3$

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(1) (a) British Patent **423,520**, February 4, 1935; (b) N. D. Scott, U. S. Patent **2,024,749**, December 17, 1935; (c) F. Straus and W. Thiel, *Ann.*, **525**, 151 (1936); (d) C. D. Nenitzescu and V. Przemetzki, *Ber.*, **69**, 2706 (1936); (e) C. D. Hurd, U. S. Patent **2,805,259**, September 3, 1957; (f) E. W. Lane, U. S. Patent **2,829,174**, April 1, 1958; (g) B. A. Vovsi and A. A. Petrov, *Zhur. obschechei khim.*, **28**, 1426 (1958).