*Analyses of products.* The 1,1-dichloro-2,2-dimethylcyclopropane (VII) and carbonates produced were analyzed by vapor-phase chromatography using a column[8] of polyethylene glycol on diatomaceous earth with helium as the eluent. The weight per cent composition of each component was obtained by determining the ratio of the individual peak areas which were calculated from the product of the peak height and the half-band width. These areas were weighted according to the areas found for standard predetermined amounts of standard samples. The yield of 2,2-dichlorobicyclo[4,1,*0*]heptane(VIII) was obtained by isolation. All samples of compound VIII had boiling points ranging over a one-degree range between b.p. 78–82.5° (15–16 mm.) and refractive indices ranging between $n_D^{25}$ 1.5001–1.5005 (reported[2a] b.p. 78–79° (15 mm.), $n_D^{23}$ 1.5014).

*Ethyl trichloroacetate*(IV) was prepared from trichloroacetic acid by the Fischer method using A.R. trichloroacetic acid[9] and absolute ethanol, with concentrated sulfuric acid as catalyst. The ethyl trichloroacetate(IV) used had b.p. 50.5–51.5° (8 mm.), $n_D^{25}$ 1.4477. (Reported[10] b.p. 58–59° (13 mm.), $n_D^{20}$ 1.4505.)

*2,2-Dichlorobicyclo[4,1,0]heptane*(VIII). Ethyl trichloroacetate(IV), 47.86 g. (0.25 mole), was added (under dry $N_2$) all at once to a cold (2.5°) mixture of commercial sodium methoxide (17.3 g., 0.32 mole) and dry cyclohexene (250 ml.). The mixture was cooled in an ice water bath and stirred (under $N_2$) for a period of 8 hr. After allowing the mixture to stand overnight, water (200 ml.) was added. The layers were separated and the aqueous phase was extracted twice with two 100-ml. portions of pentane. The organic layers were combined and dried ($MgSO_4$). The dried solution was filtered and concentrated. Distillation of the residue yielded 32.6 g. (79%, based on ethyl trichloroacetate) of 2,2-dichlorobicyclo[4,1,0]heptane(VIII), b.p. 81.5–82.5° (16 mm.), $n_D^{25}$ 1.5004 (reported[2a] b.p. 78–79° (15 mm.), $n_D^{23}$ 1.5014).

All the reactions were run in essentially the same manner as this experiment. Reactions with isobutylene were started in a dry ice bath and once the ester IV had been introduced, the mixture was allowed to reflux (at −6°).

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[8] Perkin-Elmer Co., Norwalk, Conn. Vapor Fractometer, Model 154-C, column K.

[9] Mallinckrodt Chemical Works, St. Louis 7, Mo.

[10] M. H. Palomaa, E. J. Salmi, and R. Korte, *Ber.*, **72**, 790 (1939).

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[CONTRIBUTION NO. 258 FROM THE DEPARTMENT OF CHEMISTRY, TUFTS UNIVERSITY]

# Pyrolysis of Allylic Acetates

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2-Acetoxy-*trans*-3-heptene and 4-acetoxy-*trans*-2-heptene have been pyrolyzed; the former pyrolyzed satisfactorily at 350°, whereas the latter required 363° for comparable pyrolysis. Both esters produced a mixture of 1,3- and 2,4-heptadiene. The evidence showed that the esters underwent thermal isomerization, and that in this isomerization the *trans*-configuration of the carbon-carbon double bond was essentially retained. The facts can be interpreted as supporting an intramolecular mechanism for the thermal rearrangement of allylic esters.

The pyrolysis of allylic acetates has been rarely used as a method for the preparation of conjugated dienes. In one of the early examples of this reaction van Pelt and Wibaut[1] found that the pyrolysis of 4-acetoxy-2-hexene gave a 66% yield of a diene which was designated as 2,4-hexadiene. Marvel and Williams[2] successfully employed the pyrolysis of 3-acetoxy-2-alkyl-1-butenes for the preparation of 2-alkyl-1,3-butadienes. And in the same laboratory 3-cyano-1,3-butadiene was obtained[3] by the pyrolysis of 3-acetoxy-3-cyano-1-butene. More recent work has indicated that where possible the pyrolysis of allylic acetates may give rise to a mixture of conjugated dienes as products. Grummitt and co-workers[4] have shown that the pyrolysis of either 1-cyclohexyl-3-acetoxy-butene or 1-cyclohexyl-1-acetoxy-2-butene produced as product a mixture of 1-cyclohexyl-1, 3-butadiene and 1-cyclohexylidene-2-butene. The mixture of dienes was explained by isomerization of either of the acetates to the other prior to pyrolysis.

Isomerization of the allylic ester during pyrolysis had been observed by Marvel and Brace.[3] Bailey and Barclay[5] reported isomerization of 1,4-diacetoxy-2-butene during pyrolysis, and Bailey and Goossens[6] have explained the obtention of 3-methylenecyclohexene from the pyrolysis of 1-cyclohexenylmethyl acetate by isomerization of the ester to 2-methylenecyclohexyl acetate before pyrolysis. Grummitt and Mandel[4] have shown that either of a pair of allylic acetates will undergo thermal rearrangement to the other. This type of isomerization also occurs with propargylic acetates, for the Landors[7] have reported the rearrangement

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[1] A. J. van Pelt, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

[2] C. S. Marvel and J. L. R. Williams, *J. Am. Chem. Soc.*, **70**, 3842 (1948).

[3] C. S. Marvel and N. O. Brace, *J. Am. Chem. Soc.*, **70**, 1775 (1948).

[4] O. Grummitt and J. Splitter, *J. Am. Chem. Soc.*, **74**, 3924 (1952); O. Grummitt and Z. Mandel, *J. Am. Chem. Soc.*, **78**, 1054 (1956).

[5] W. J. Bailey and R. Barclay, Jr., *J. Org. Chem.*, **21**, 328 (1956).

[6] W. J. Bailey and J. C. Goossens, *J. Am. Chem. Soc.*, **78**, 2804 (1956).

[7] P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 1015 (1956).

of propargylic acetates on pyrolysis to an allenic system. The ease with which this isomerization occurs does not appear to have been always properly appreciated, and proper precaution should be observed in the esterification of allylic alcohols. Heilbron *et al.*[8] found that 3-acetoxy-1,4-hexadiene when warmed to 100° in acetic anhydride isomerized to 5-acetoxy-1,3-hexadiene. Burton[9] reported another allylic ester which isomerized when heated with acetic anhydride.

In the present work 2-acetoxy-*trans*-3-heptene and 4-acetoxy-*trans*-2-heptene were pyrolyzed. The 2-acetoxy compound pyrolyzed satisfactorily (about 50% pyrolysis) at 350°, but to achieve comparable pyrolysis with the 4-acetoxy compound a temperature of 363° was required. Under the experimental conditions employed the ester had a contact time of 3.8 sec. In each case diene was obtained in about an 80% yield, and this diene proved to be a mixture of 1,3- and 2,4-heptadiene. The 2-acetoxy compound gave a 36% yield of the 1,3-diene and a 32% yield of the 2,4-diene, whereas from the 4-acetoxy compound a 44% yield of the 2,4-diene and a 30% yield of the 1,3-diene were obtained. The two dienes could not have been formed by isomerization of one to the other, for when the 2,4-diene was subjected to the pyrolysis conditions used for the esters the diene underwent almost no isomerization to the 1,3-diene. The 1,3-diene when pyrolyzed did isomerize to the 2,4-diene, but the isomerization was not extensive enough to account for the yield of 2,4-diene obtained from the 2-acetoxy compound. Moreover, the 1,3-diene on pyrolysis gave no *trans, trans*-2,4-heptadiene, and this geometric isomer constituted about half of the 2,4-diene obtained by ester pyrolysis. The obtention of the mixture of dienes can only be explained by some of the ester's isomerizing before pyrolysis.

That these allylic esters did isomerize under the pyrolysis conditions was shown by examination of the unpyrolyzed ester recovered from the pyrolysis condensate. The 2-acetoxy and 4-acetoxy compounds had the same boiling point, the same refractive index, and the same retention time in gas chromatography. The infrared absorption of the two esters were somewhat different, and this enabled one to determine the approximate composition of a mixture of the esters. In this way the ester recovered from the pyrolyzate of each ester was found to contain 60 ± 5% of the 2-acetoxy compound and 40 ± 5% of the 4-acetoxy compound.

From the yields of crystalline maleic anhydride adducts the 1,3-diene obtained from either ester was found to be predominantly the *trans*-isomer, and the 2,4-diene in each case was about 50% of the *trans, trans*-configuration. One might expect that the loss of acetic acid from the 4-acetoxy-*trans*-2-heptene would give rise to approximately equal amounts of the *trans, trans*- and *trans, cis*-isomers. The above-mentioned facts indicated that in the rearrangement of the *trans*-allylic esters the *trans*-configuration of the double bond was essentially retained. This conclusion is strengthened by the gas chromatographic analysis of the ester recovered from the pyrolysis of the 4-acetoxy compound. The esters when initially prepared were found to contain on gas chromatography 96–97% of a component of retention time 7.83 minutes and 1.42–2.3% of a component of retention time 6.54 minutes. Because of the proximity of the 6.54-component to the main component and the marked differences between these retention times and those of the other minor constituents, the 6.54-component was believed to be the *cis*-ester. Careful distillation of the recovered ester gave fractions that were essentially constant boiling and essentially of constant refractive index. Gas chromatography of the combined fractions showed the recovered ester to be 83% of the 7.83-component and 15% of the 6.54-component. If the 6.54-component were a compound not closely related to the *trans*-esters, one would expect that the component in a mixture containing 15% of it could have been detected during the distillation. The above facts would support the essential retention of configuration of a *trans*-double bond during thermal isomerization of an allylic acetate.

The retention of optical activity during the thermal rearrangement of allylic systems[10] has been the prime evidence for the proponents of an intramolecular, essentially non ionic mechanism for this rearrangement. More recent evidence[11] has given support to this viewpoint. When this intramolecular conception is applied to the thermal isomerization of allylic esters, the intermediate complex is one where the carbonyl oxygen atom approaches within bond forming distance of the $\alpha$-carbon atom of the allylic system. In an allylic acetate system the molecule may assume a conformation where the carbonyl oxygen atom approaches the $\alpha$-carbon atom from one side, or it may assume a conformation where the approach is to the opposite side of the $\alpha$-carbon atom. In the one case the hydrogen atoms on the $\alpha$-and $\beta$-carbon atoms of the allylic system are *cis* (*cis*-conformation), whereas in the other these hydrogen atoms are *trans* (*trans*-conformation). In the *cis*-conformation there is considerable interaction of the alkyl group on the $\alpha$-carbon atom and the hydrogen atom on the $\alpha$-carbon atom. This is not the case in the *trans*-conformation. This interaction

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[8] I. M. Heilbron, E. R. H. Jones, J. T. McCombie, and B. C. L. Weedon, *J. Chem. Soc.*, **147,** 88 (1945).

[9] H. Burton, *J. Chem. Soc.*, **130,** 1650 (1928).

[10] M. P. Balfe and J. Kenyon, *Trans. Faraday Soc.*, **37,** 721 (1941).

[11] E. A. Braude, D. W. Turner, and E. S. Waight, *J. Chem. Soc.*, 2396 (1958); E. A. Braude and D. W. Turner, *J. Chem. Soc.*, 2404 (1958).

in the *cis*-conformation is true with both esters. The models would indicate that the *trans*-conformation is the preferred one when the ester undergoes isomerization. This explains the fact that the *trans*-configuration of the double bond was essentially retained when the allylic acetates underwent thermal isomerization, and this fact can be interpreted as supporting the concept of an intramolecular mechanism for this rearrangement.

## EXPERIMENTAL

*Chemicals. Methyl iodide* (Matheson, Coleman and Bell) was distilled through an 18-plate, Fenske column, and the material of b.p. 43°/758 mm. collected.

*n-Propyl chloride* (Matheson, Coleman and Bell)was distilled as was the methyl iodide, and the material of b.p. 47°/761 mm. collected.

*Crotonaldehyde* (Matheson, Coleman and Bell) was distilled under nitrogen through the Fenske column, and the material of b.p. 103–104°/756 mm. collected. The aldehyde was used immediately after distilling. Crotonaldehyde has the *trans*-configuration at its double bond.[12]

*trans-2-Hexenal* was prepared from 1,1,3-triethoxyhexane[13] by the method of Hoaglin and Hirsh.[14] The aldehyde was distilled from a Claisen flask having a distilling arm (25 mm. O.D. × 245 mm.) packed with $^1/_8$ inch glass helices. The material collected (235 g., 73% yield) had b.p. 29–30°/7 mm., $n_D^{25}$ 1.4433. This should be the *trans*-isomer.[15] The infrared absorption (very strong absorption at 10.3 μ and little absorption in the 12–14 μ range) of the material was in keeping with the assignment of the *trans*-configuration to the double bond.[16] In the ultraviolet the material had $\lambda_{\text{isooctane}}^{\text{max.}}$ 215 mμ, $\epsilon$ 17,300.

*trans-Hept-2-en-4-ol* was prepared by the interaction of crotonaldehyde and *n*-propyl Grignard reagent, hydrolysis of the reaction mixture with aqueous ammonium chloride and distillation of the crude material from the modified Claisen flask. The product (265 g., 78% yield) had b.p. 58–59°/11 mm., $n_D^{25}$ 1.4348.

*trans-Hept-3-en-2-ol* was prepared from *trans*-2-hexenal and methyl Grignard reagent by the procedure outlined for the preceding alcohol. The material (259 g., 95% yield) had b.p. 63–64°/14 mm., $n_D^{25}$ 1.4346. The infrared absorption of the compound (very strong band at 10.35 μ and little absorption in the 12–14 μ region) was consistent with the assignment of the trans-configuration.[16]

*4-Acetoxy-trans-2-heptene* was obtained from the alcohol by the esterification procedure of Heilbron *et al.*,[8] which does not effect rearrangement of the molecule. The ester was distilled from the modified Claisen flask, and the ten fractions (190 g., 91% yield) collected as product distilled at 63.5–64.0°/11 mm.; all fractions had $n_D^{25}$ 1.4226. The infrared curve (strong absorption at 10.35 μ and little absorption in the 12–14 μ region) again indicated the material to be of the *trans*-configuration and the essential absence of the *cis*-isomer. Gas chromatography (polyethylene glycol 400 column) of the ester showed it to be 96.7% of a component of retention time 7.83 minutes (minutes from air peak), 1.4% of a component of retention time 6.54 minutes and four other components each present to the extent of less than 1%. The 7.83-component must be the *trans*-ester. Because of the nearness of its retention time to that of the main component and the wide difference between the retention times of the four minor components and the other two components, the 6.54-component was believed to be a small amount of the *cis*-ester.

*2-Acetoxy-trans-3-heptene* was prepared from the corresponding alcohol by the procedure[8] indicated above. Nine fractions of ester (318 g., 90% yield) were obtained at b.p. 68.0–68.5°/14 mm.; each fraction had $n_D^{25}$ 1.4226. The infrared curve of this ester was quite similar to that of the 4-acetoxy-*trans*-2-heptene, but there were definite differences. Strong absorption at 10.35 μ and little absorption in the 12–14 μ region substantiated the *trans* assignment. Gas chromatography of the ester indicated it to be 96.4% of a component of retention time 7.83 minutes, 2.3% of a component of retention time 6.54 minutes, and two other components of very short retention times each present to the extent of less than 1%. The 7.83- and 6.54-component were believed to be the *trans*- and *cis*-ester, respectively.

*1,3-Heptadiene.* The diene from various preparations[17] was combined and distilled through a Nester spinning band column (7 mm. I.D. × 600 mm.). The fractions of b.p. 66.0–66.2°/235 mm., $n_D^{25}$ 1.4428–1.4433 were accepted as the diene. The infrared curve of this material had very strong absorption at 10.0 and 11.17 μ, strong absorption at 10.53 μ and little absorption in the 12–14 μ region. Gas chromatography (Apiezon L and tricresyl phosphate columns) showed the material to be 99.0% of a component of relative retention time 0.52 (relative to *n*-octane). Preparation (one hour reflux of reactants in benzene) of a maleic anhydride adduct of the diene gave a 62% yield (one crystallization, 81% crude yield) of derivative, m.p. 71.8–72.3°. The infrared data and the yield of adduct indicated[16,18] that the diene was primarily the *trans*-isomer.

*2,4-Heptadiene.* Various samples of the diene[17] were combined and distilled through the spinning-band column. The fraction of b.p. 60.0–60.2°/140 mm., $n_D^{25}$ 1.4543–1.4549 were accepted as the diene. Gas chromatography (Apiezon L) showed the material to be 100% of a component of relative retention time 0.70. The tricresyl phosphate column indicated two components (91.3% of one and 8.7% of another). The diene gave a 26% yield (one crystallization, 46% crude yield) of maleic anhydride adduct, m.p. 72.2–73.0°. The infrared curve of the material was a good check with that reported earlier,[17] and there was a peak at 13.1 μ which was indicative of a *cis*-configuration.[16] The isomer of *trans-trans* configuration of a conjugated diene is the one which should give[19] the maleic anhydride adduct readily, and the data would indicate that this diene was not particularly rich in this isomer.

*Preliminary pyrolysis experiments.* The apparatus was essentially that described by Bailey *et al.*,[20] except that a wet test meter was attached to the Dry Ice-cooled condenser. Dry, oxygen-free nitrogen was passed through the apparatus at different rates in different experiments and a rate of 18.5 l./hr. selected as the desirable one. This rate of nitrogen flow was used in all pyrolyses reported and gave a

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[12] W. G. Young, *J. Am. Chem. Soc.*, **54**, 2498 (1932).

[13] We are indebted to the Carbide and Carbon Chemicals Company for this chemical.

[14] R. I. Hoaglin and D. H. Hirsh, *J. Am. Chem. Soc.*, **71**, 3468 (1949).

[15] M. Jacobson, *J. Am. Chem. Soc.*, **78**, 5084 (1956). A private communication from Dr. Jacobson stated that the 2-hexenal supplied by Carbide and Carbon Chemicals Company was identical with the aldehyde obtained by converting the carboxyl group of *trans*-2-hexenoic acid (prepared from *n*-butyraldehyde and malonic acid by a Doebner reaction which gives rise to a *trans*-configuration at the double bond) to an aldehyde group.

[16] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley and Sons, Inc., New York, 1958, pp. 45–48.

[17] F. L. Greenwood and J. A. Sedlak, *J. Org. Chem.*, **22**, 776 (1957).

[18] D. Craig, *J. Am. Chem. Soc.*, **72**, 1678 (1950).

[19] *Cf.* ref. 15 and refs. cited therein.

[20] W. J. Bailey, J. Rosenberg, and L. J. Young, *J. Am. Chem. Soc.*, **76**, 2251 (1954).

contact time[21] of 3.8 sec. for the ester in the pyrolysis tube. The top of the helices had to be sufficiently far inside the furnace so that they were hot enough to vaporize the ester (b.p. 173°/762 mm.) immediately. Otherwise, polymeric material formed at the top of the helices. In these experiments 10.0 g. of ester was pyrolyzed, and the percent of pyrolysis calculated from the acetic acid formed. Table I gives the results of these experiments.

TABLE I

| Ester Pyrolyzed | Temp., °C. | Addition Rate of Ester, g./min. | Percent Pyrolysis |
|---|---|---|---|
| 2-Acetoxy-3-heptene | 350 | 0.34 | 56 |
| | 350 | 0.64 | 44 |
| | 375 | 0.80 | 72 |
| 4-Acetoxy-2-heptene | 350 | 0.35 | 28 |
| | 363 | 0.34 | 52 |
| | 363 | 0.67 | 46 |
| | 375 | 0.34 | 73 |

The interesting finding in these experiments was the rather small increase in temperature necessary to obtain pyrolysis of the 4-acetoxy compound comparable to that obtained with the 2-acetoxy compound at 350°.

From these experiments it was decided to use an addition rate of 0.34 g./min. for the ester. When larger quantities of ester were pyrolyzed, it was found that the degree of pyrolysis was somewhat less than indicated in Table I.

*Pyrolysis of 2-acetoxy-trans-3-heptene.* A trap containing 130 ml. of 1$N$ sodium hydroxide was placed between the Dry Ice-cooled trap and the wet test meter. The furnace was maintained at 350° during the pyrolysis of 93.7 g. (0.600 mole) of ester which was added at the rate of 0.34 g./min. As the helices were just slightly discolored after the pyrolysis, very little carbonization had occurred.

At the conclusion of the pyrolysis carbonate was determined in the sodium hydroxide solution by precipitating and weighing as barium carbonate. After correcting for a blank (0.13 mmole), barium carbonate equivalent to 2.22 mmoles of carbon dioxide was found. This small amount of carbon dioxide was evidence against the formation of any appreciable amount of acetate radical during the pyrolysis.

The condensate from the pyrolysis was diluted with pentane, and this solution (260 ml.) was extracted with six 75 ml. portions of water. The combined aqueous extracts were made to volume in a 500 ml. volumetric flask, and titration of aliquots with standard base indicated the formation of 276 ml. of acetic acid during the pyrolysis. From this value, the ester was pyrolyzed to the extent of 46%.

The organic materials were always kept under a nitrogen atmosphere and some hydroquinone was present in the liquid. After drying over freshly heated sodium sulfate, the pentane was removed from the pentane solution through the Fenske column. The distillation was discontinued when the pot temperature reached 80°. The residue was distilled through the spinning-band column. The diene and unpyrolyzed ester were rather rapidly separated by gradually lowering the pressure in the system and slowly increasing the temperature of the distilling flask. This process was discontinued when the pressure had been lowered to 11 mm. and the bath temperature of the distilling flask raised to 76°. The more volatile material was collected in Dry Ice-cooled traps. This material was then stored in the refrigerator.

The unpyrolyzed ester was distilled through the spinning-band column and eighteen fractions (total wt. 46.88 g.) were collected over the boiling range 61.2–62.0°/12 mm. Each fraction had $n_D^{25}$ 1.4225 or 1.4226. This ester represents 93% of the possible recoverable ester.

Infrared analysis proved this recovered ester to contain both the 4-acetoxy and 2-acetoxy compounds. The infrared curves of the two esters were quite similar. However, the 2-acetoxy compound had peaks at 9.6 and 11.9 $\mu$ which were not present in the absorption curve of the 4-acetoxy compound, and the latter had peaks at 9.8 and 12.1 $\mu$ which were not present in the curve of the 2-acetoxy compound. The 9.6 and 9.8 $\mu$ peaks overlapped too much to be useful for quantitative analysis; the overlap of the 11.9 and 12.1 $\mu$ peaks was such that these could be used for an approximate analysis. Determination of the infrared absorption in the 11–13 $\mu$ region of a series of known mixtures of the two esters indicated that one could determine the composition of a mixture of the esters with an error of about ±5%. The above-mentioned ester fractions were combined, and infrared analysis of this mixture indicated it to be 60 ± 5% of the 2-acetoxy compound and 40 ± 5% of the 4-acetoxy compound. Clearly, both esters were present in the recovered ester, and this indicated that the ester which did not pyrolyze did undergo rearrangement.

The pentane was removed from the pentane-diene solution through the spinning-band column, and the diene then carefully fractioned. The total distillate collected (19.82 g.) represented a 75% yield of diene (based on the ester actually pyrolyzed). Of the diene 9.66 g. (36% yield, ten fractions, b.p. 53.0–54.5°/152 mm., $n_D^{25}$ 1.4410–1.4425) was accepted as 1,3-heptadiene, and 8.39 g. (32% yield, five fractions, b.p. 61.4–62.4°/152 mm., $n_D^{25}$ 1.4531–1.4540) was accepted as 2,4-heptadiene.

The material accepted as the 1,3-diene gave a 78% yield (after one crystallization, 94% crude yield) of maleic anhydride adduct, m.p. 72.2–72.8° (no m.p. depression when mixed with an authentic sample). The infrared absorption of this diene was an excellent match with that of the 1,3-heptadiene reported under *Chemicals.* Gas chromatography proved the material to be 98.4% of a component of relative retention time 0.53. The data indicated that this diene was principally *trans*-1,3-heptadiene.

The material accepted as the 2,4-diene gave a 48% yield (after one crystallization, 61% crude yield) of maleic anhydride adduct, m.p. 72.8–73.3° (no depression with authentic sample). The infrared absorption of this diene checked well with that of the 2,4-diene reported under *Chemicals.* Gas chromatography showed the material to be 99.7% of a component of relative retention time 0.72. These data indicated that this 2,4-diene was approximately 50% *trans,trans*-isomer.

*Pyrolysis of 4-acetoxy-trans-2-heptene.* The pyrolysis and work-up procedure were the same as those described for the preceding ester, except that the furnace was kept at 370°. At the conclusion of the pyrolysis the helices in the pyrolysis tube were only slightly discolored. The ester (132.5 g., 0.848 mole) on pyrolysis liberated 468 me. of acetic acid, which indicated pyrolysis to the extent of 55%. The barium carbonate obtained from the trap containing the alkali solution showed the formation of 0.21 mmole of carbon dioxide.

Distillation of the unpyrolyzed ester gave 54.57 g. of ester, b.p. 64.0–65.7°/13 mm., $n_D^{25}$ 1.4223–1.4226 (21 fractions). This ester corresponded to 92% of the possible recoverable ester. In the infrared curves of various fractions the 10.37 $\mu$ band (*trans* double bond) was not as strong in the first few fractions as it was in later fractions, and the 13.7 $\mu$ band (*cis* double bond) was fairly strong (42% transmission; 2% transmission at strongest band of the curve) in the early fractions and diminished in later fractions. These infrared spectra indicated that the *cis*-ester tended to concentrate in the early ester fractions. Infrared analysis of the combined ester fractions showed it to be 60 ± 5% of the 2-acetoxy compound and 40 ± 5% of the 4-acetoxy compound. Gas chromatography of the combined ester fractions showed it to be 83.1% of a component of retention

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(21) C. D. Hurd and H. T. Bollman, *J. Am. Chem. Soc.*, **55**, 699 (1933).

time 7.83 minutes and 15.4% of a component of retention time 6.54 minutes. These data indicated that the unpyrolyzed ester was a mixture of the two structural isomers, and that the *trans*-esters predominated.

The total diene distillate (36.01 g.) calculated to an 80% yield. The material (13.67 g., 30% yield) accepted as 1,3-heptadiene had b.p. 54.2–54.7°/152 mm., $n_D^{25}$ 1.4422–1.4426 (12 fractions), and the fractions (19.94 g., 44% yield) accepted as 2,4-diene had b.p. 61.9–62.5°/153 mm., $n_D^{25}$ 1.4534–1.4542 (11 fractions).

The 1,3-diene gave a 73% yield (after one crystallization, 87% crude yield) of maleic anhydride adduct, m.p. 72.2–73.0° (no depression with an authentic sample). The infrared curve matched well with that of the 1,3-diene reported under *Chemicals,* and gas chromatography showed the material to be 98.9% of a component of relative retention time 0.53. These data proved the diene to be primarily the *trans*-1,3-heptadiene.

The 2,4-diene on gas chromatography was shown to be 100% of a component of relative retention time 0.69. The infrared absorption agreed well with that of the 2,4-diene reported under *Chemicals.* The material gave a 54% yield (after one crystallization, 65% crude yield) of maleic anhydride adduct, m.p. 72.8–73.2° (no depression with an authentic sample). These data indicated that the diene must be approximately 50% *trans,trans*-2,4-heptadiene.

*Pyrolysis of 1,3-heptadiene.* The apparatus and conditions for this experiment were the same as those used for the ester pyrolyses. The furnace was kept at 363°. There was no discoloration of the helices at the conclusion of the pyrolysis. After pyrolysis of the diene (20.97 g., *cf. Chemicals*) the condensate was rinsed with pentane into a flask and distilled through a spinning-band column. After removal of the pentane, fractions totalling 18.19 g. (87% recovery of the diene pyrolyzed) were collected. Of this material 13.55 g. (nine fractions, b.p. 65.4–66.5°/233 mm., $n_D^{25}$ 1.4413–1.4429) was accepted as 1,3-heptadiene, and 2.69 g. (five fractions, b.p. 68.5–69.1°/194 mm., $n_D^{25}$ 1.4563–1.4567) was accepted as 2,4-heptadiene. The absence of residue in the distilling flask indicated the absence of polymerization of the diene during the pyrolysis.

The material accepted as the 1,3-diene had an infrared curve which checked well with that of the starting diene. Gas chromatography showed the material to be 97.4% of a component of relative retention time 0.51 and 2.3% of a component of relative retention time 0.72. The material gave a 77% yield (after one crystallization, 97% crude yield) of maleic anhydride adduct, m.p. 71.8–72.4° (no depression with an authentic sample). These data proved this recovered diene to be predominately *trans*-1,3-heptadiene.

The material accepted as the 2,4-diene on gas chromatography was found to be 99.7% of a component of relative retention time 0.71 and 0.3% of a component of relative retention time 0.52. The material gave no Diels-Alder adduct with maleic anhydride. In the ultraviolet it had $\lambda_{max}^{EtOH}$ 230.5 mμ, $\epsilon$ 22,200. The infrared absorption agreed well with that of the 2,4-diene (*cf. Chemicals*). These data indicated the material to be 2,4-heptadiene and the absence of the *trans-trans* isomer.

The above data showed that under the conditions of pyrolysis of the ester the 1,3-diene (mostly *trans*) did isomerize to the 2,4-diene, but it did not isomerize to any significant extent and it did not isomerize to form any *trans,trans*-2,4-diene.

*Pyrolysis of 2,4-heptadiene.* The diene (16.07 g., *cf. Chemicals*) was pyrolyzed as described above for the 1,3-diene. The helices were not discolored after the pyrolysis. Distillation of the condensate gave 11.86 g. of material (74% recovery of the material pyrolyzed). The absence of residue in the distilling flask indicated the absence of polymerization of the diene during the pyrolysis. The first fraction (0.45 g.) had $n_D^{25}$ 1.4403, and the remainder of the distillate (11 fractions) had b.p. 57.6–59.3°/134 mm., $n_D^{25}$ 1.4531–1.4556. Gas chromatography of the first fraction showed it to be 40.1% of a component of relative retention time 0.52, 48.5% of a component of relative retention time 0.68 and 11.4% of various components of relative retention time 0.03–0.43. The infrared curve of this material had strong bands at 10.15 and 11.10 μ, which were indicative of a terminal methylene group. The remainder of the distillate proved to be the 2,4-diene. Gas chromatography showed it to be 99% of a component of relative retention time 0.69. It gave a 31% yield (first crystallization, 49% crude yield) of maleic anhydride adduct, m.p. 71.6–72.4° (no depression with an authentic sample), and the infrared spectrum was identical with that of the starting material.

These data showed that the 2,4-diene on pyrolysis isomerized to the 1,3-diene to a very slight extent.

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