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ALLENES. IV. THE REACTION OF SOME ALLENES WITH LEAD TETRAACETATE

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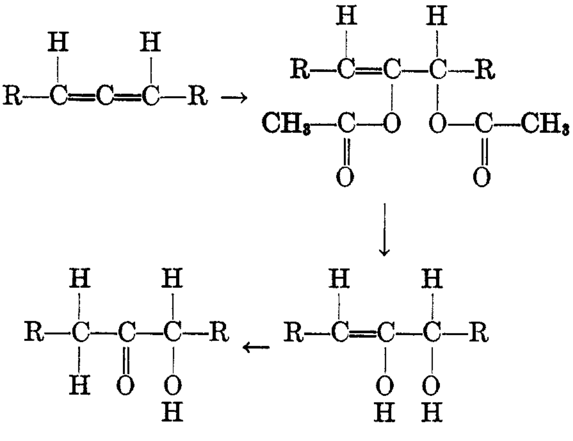
The action of lead tetraacetate upon ethylene compounds has been extensively investigated. From the results reported, especially by Dimroth and Schweizer (1) and by Criegee, Kraft, and Rank (2), it is evident that the reaction generally proceeds in several directions but in many instances consists mainly in the addition of a pair of acetoxy radicals to the double bonds. Saponification of the diacetyl derivatives furnishes the corresponding glycols. There is in the literature no report of the reaction of lead tetraacetate with a compound containing the cumulated system of double bonds.

In connection with our investigations on the relation of these compounds to pyrethrone, it was of interest to apply to them the reaction with lead tetraacetate as a method for identifying the cumulated system. It is evident that if one of a pair of adjacent double bonds in a compound were saturated by addition of two acetoxy groups, saponification of the diacetyl derivative would result in the formation of an *alpha*-hydroxy enol, which would rearrange to an *alpha*-hydroxy ketone.



This series of reactions was applied to 1-phenyl-1,2-butadiene (3), 1-cyclohexyl-2,3-pentadiene (4), and 2,3-pentadiene (5). The method employed consisted in agitating an acetic acid solution of the hydrocarbon with the calculated quantity of lead tetraacetate until the reagent had been used up. The temperature was kept at 40° or slightly higher, depending on which hydrocarbon was being treated. Two methods of isolation recommended by Criegee and co-workers (2) were employed. If no water-soluble products were anticipated, part of the acetic acid was removed under reduced pressure, water was added, and the reaction-products were extracted with ether (method A); if water-soluble products were expected, the acetic acid solution was diluted with absolute ether and the lead acetate removed by filtration, after which the solvents were removed, the residue again dissolved in ether, and the remaining acid and lead acetate removed with the minimum of water and bicarbonate solution (method B).

When 1-phenyl-1,2-butadiene was treated with lead tetraacetate, the reaction-product isolated by method A was a sirup which in a short time crystallized to a large extent. This crystalline reaction-product on analysis proved to be a diacetoxy compound corresponding to the empirical formula $C_{14}H_{16}O_4$, which may be either 1-phenyl-2,3-acetoxy-1-butene, $C_6H_5CH{=}C(CH_3CO_2)CH(CH_3CO_2)CH_3$ (I), or 1-phenyl-1,2-acetoxy-2-butene, $C_6H_5CH(CH_3CO_2)C(CH_3CO_2){=}CHCH_3$ (II), the former being more probable, since it has been shown that halogens add to 1-phenyl-1,2-butadiene in the 2,3 position (6). Furthermore, the crystalline diacetoxy derivative may be either the cis or the trans form, and its geometric isomer may be present in the noncrystalline part of the reaction-product, as will be referred to later. The crystalline compound still contained one double bond, since hydrogenation resulted in a dihydro derivative. The original diacetoxy compound was unstable in the presence of alkalies, but complete saponification could be accomplished smoothly by boiling in ethanolic potassium acetate solution.

The reaction-product, however, proved to be a ketone of formula $C_{10}H_{10}O$, instead of the expected hydroxy ketone of formula $C_{10}H_{12}O_2$. The empirical formula was established by analysis of the ketone itself, its semicarbazone, and its *p*-nitro- and 2,4 dinitro- phenylhydrazones. The formula $C_{10}H_{10}O$ corresponds to that of a phenylbutenone. Two compounds of this category are well known—1-phenyl-2-butene-1-one, $C_6H_5COCH{=}CHCH_3$ (III), and 1-phenyl-1-butene-3-one, $C_6H_5CH{=}CHCOCH_3$ (IV)—both of which are unlikely to result from I or II, for either of those compounds should furnish a ketone with the carbonyl in position 2. Moreover, both III and IV are definitely excluded by the properties of their derivatives. There still remained the possibility of the ketone being the unknown 1-phenyl-3-butene-2-one, $C_6H_5CH_2COCH{=}CH_2$ (V), but this is also excluded because vinylalkyl ketones form characteristic semicarbazide-semicarbazones and they are easily hydrogenated to ethylalkyl ketones. The ketone resulting from the saponification of the diacetoxy derivative I or II does not hydrogenate like an unsaturated compound. The hydrogenation proceeds slowly, and when the required volume of hydrogen is absorbed the product is a mixture consisting of the unchanged ketone, which may be isolated as the semicarbazone, and products of deep-seated hydrogenation. It may be concluded, therefore, that the ketone does not contain an unsaturated linkage but probably a cyclic structure in the side chain. Oxidation would be expected to settle the question whether there were one or two points of attachment to the benzene ring. In the first case benzoic acid would result; in the second, phthalic acid. Permanganate oxidation furnished benzoic acid in nearly quantitative yield, thus excluding a double attachment to the benzene ring, and acetic acid was the only other oxidation-product. Hence the ketone of formula $C_{10}H_{10}O$ contains a methyl as well as a phenyl group, and formula V is again excluded.

There is now only one possible structural formula remaining which corresponds to all the facts, namely, 1-phenyl-3-methyl-cyclopropane-2-one,  $\underset{HCCH_3}{C_6H_5CH\text{—}CO}$ (VI). A compound of this formula would result by ring closure with elimination of water from the hydroxy ketone formed as the intermediate compound on saponification of either I or II. It seems most probable that formula I would best lend itself to dehydration after saponification, owing to the presence of the methylene group adjacent to the phenyl group. Subsequent experience showed that this ring closure does not occur when other allenes are subjected to the series of reactions just described.

The noncrystalline products of the reaction of lead tetraacetate on 1-phenyl-1,2-butadiene probably contain some of the geometric isomer of the crystalline diacetoxy compound, I or II, for on saponification they furnish considerable amounts of the ketone VI. Before saponification a small quantity of the ketone itself is also present, and it was obtained in the lowest-boiling fraction when the noncrystalline products were distilled.

When 1-cyclohexyl-2,3-pentadiene was treated with lead tetraacetate and the products were isolated by method B, no primary crystalline compounds were obtained. A considerable quantity of unchanged hydrocarbon was recovered on distillation of the reaction-product. Acetyl determinations indicated that the higher-boiling constituents of the reaction-product were mixtures. A fraction could be obtained, however, with the acetyl content of a diacetoxycyclohexylpentene, and saponification of this fraction yielded a material with the properties of a hydroxy ketone. On treatment with *p*-nitrophenylhydrazine in boiling ethanol solution, it yielded a crystalline compound, which on analysis proved to be the osazone that would result from a cyclohexylhydroxypentanone. Therefore, no ring formation had occurred during saponification of the diacetyl derivative, as in the case of 1-phenyldiacetoxybutene.

The reaction between 2,3-pentadiene and lead tetraacetate proceeded in a manner analogous to the one just described. The reaction-products were treated according to method B, but on removal of the solvents considerable quantities of volatile products distilled with them, giving a yellow distillate from which nothing could be isolated. The residue was distilled at low pressure, yielding a fraction with the acetyl content corresponding to a diacetoxypentene. Saponification could be accomplished by boiling with potassium acetate in ethanol solution, but better results were obtained by boiling with ethanolic hydrochloric acid. The yellow solution was then distilled at atmospheric pressure. An aliquot of the yellow distillate, when treated with *p*-nitrophenylhydrazine, yielded a crystalline derivative which from analysis was shown to be the *p*-nitrophenylosazone corresponding to a hydroxypentanone.

Another aliquot of the distillate was treated with semicarbazide hydrochloride and furnished the disemicarbazone of a pentandione.

The volatile saponification-product of the diacetoxy derivative therefore consists of a mixture of hydroxy ketone and its oxidation-product, the diketone.

When pyrethrone was treated with lead tetraacetate, the reaction was very rapid. The product was isolated by method B, and from it nearly half of the pyrethrone employed was recovered unchanged on distillation. The remaining portion was a high-boiling viscous resin, which on saponification yielded no ketonic product. Its cyclopentenone component seems to be more susceptible to the action of lead tetraacetate than is the side chain and undergoes deep-seated decomposition.

EXPERIMENTAL

1-Phenyldiacetoxybutene (I or II). A solution of 5.9 g. of 1-phenyl-1,2-butadiene (3) in 40 cc. of glacial acetic acid was treated with 23 g. of lead tetraacetate, which was added in several portions. The temperature was maintained at 50–55°, and the suspension was agitated until the reaction was complete. The solution was concentrated under reduced pressure and then diluted with water, and the reaction-product was extracted with ether (method A). The ethereal solution was washed with water and then with sodium bicarbonate solution, dried, and the solvent removed, leaving a sirupy residue which promptly crystallized in part.

The crystalline reaction-product, consisting of heavy colorless prisms, was separated from the mother liquor by filtration on silk and washed with petroleum ether. The yield was 4.3 g. It was recrystallized from ligroin and melted at 73–74°.

Anal. Calc'd for $C_{14}H_{16}O_4$: C, 67.74; H, 6.48; 2 CH_3CO, 34.6.
Found: C, 67.99; H, 6.41; CH_3CO, 36.0.

The liquid portion of the reaction-products (4.6 g.) was distilled at 10 mm. pressure, yielding 0.45 g., b.p. 75–100°; 1.1 g., b.p. 125–135°, and 2.25 g., b.p. 140–160°. The highest-boiling fraction yielded a small quantity of the crystalline reaction-product melting at 73°, which was isolated by filtration and washing with petroleum ether. The remaining liquid product was analyzed for acetyl.

Anal. Calc'd for $C_{14}H_{16}O_4$: 2 CH_3CO, 34.6. Found: CH_3CO, 28.7.

Hydrogenation of 1-phenyldiacetoxybutene. Two grams of substance in about 15 cc. of glacial acetic acid was hydrogenated with platinum oxide catalyst, and absorbed 350 cc. of hydrogen in 35 minutes (calc'd for H_2, 366 cc.). The reaction-product was isolated by dilution of the acetic acid solution with water and extraction with ether. The ether residue was a mixture, which, when distilled at 9 mm., separated into two fractions, a small quantity of material of low but indefinite boiling point and a higher-boiling fraction. The latter was redistilled, yielding 1.5 g. of liquid boiling at 145–146° (9 mm.). Analysis indicated it to be *l*-phenyldiacetoxybutane.

Anal. Calc'd for $C_{14}H_{18}O_4$: C, 67.20; H, 7.21.
Found: C, 67.68; H, 7.53.

The low-boiling fraction appears from analysis to consist of more completely hydrogenated products.

Anal. Found: C, 82.64; H, 12.00.

Saponification of 1-phenyldiacetoxybutene (I or II). One gram of 1-phenyldiacetoxybutene was dissolved in 10 cc. of 90% ethanol containing 1.2 g. of potassium acetate, and the solution was boiled under reflux for 5 hours. The solution was then diluted with water and extracted with ether. The ethereal solution was washed with water to remove the ethanol, and dried. The solvent was removed, and the residue (0.7 g.), on standing, deposited a small quantity of crystals, which were separated by dissolving the liquid portion in petroleum ether. The crystalline material (0.15 g.) was identified as starting material. The liquid portion, after removal of the solvent, yielded on distillation 0.35 g. of product boiling at about 80° (0.7 mm.).

The semicarbazone was prepared in the usual manner in pyridine aqueous ethanol solution. The crystalline material that separated in a short time was recrystallized from methanol; it melted at 202–203°.

Anal. Calc'd for $C_{11}H_{13}N_3O$: C, 65.01; H, 6.44; N, 20.68.
Found: C, 65.10; H, 6.45; N, 20.47.

The *p*-nitrophenylhydrazone was prepared by adding 0.1 g. of distillate in 1 cc. of alcohol to 0.1 g. of *p*-nitrophenylhydrazine hydrochloride in 1 cc. of water. Crystallization began at once, and the crystals, after standing for some time, were removed by filtration and washed with 50% ethanol. The substance, when recrystallized from about 4 cc. of ethanol, melted at 175–176°; yield, 0.16 g.

Anal. Calc'd for $C_{16}H_{15}N_3O_2$: C, 68.32; H, 5.38; N, 14.94.
Found: C, 68.35; H, 5.23; N, 15.39.

In a second experiment the saponification of the 1-phenyldiacetoxybutene was accomplished completely by increasing the boiling time, and the reaction-product was converted directly into the semicarbazone. Two and five-tenths grams of the diacetoxy compound in 25 cc. of 90% ethanol containing 3 g. of potassium acetate was boiled for 10 hours under reflux. Two grams of pyridine and 2.5 g. of semicarbazide hydrochloride in 3 cc. of water were added to the solution. The separated potassium chloride was not removed, but the reaction-mixture was allowed to stand overnight, after which time the crystallization was complete. The solid material was removed by filtration and washed with a little ethanol. The salts were removed by washing with water, leaving the insoluble semicarbazone. The ethanolic mother liquor furnished a small quantity of crystalline material on dilution with water, and this was combined with the main portion, and the whole washed with ether. The ether washings, on evaporation, yielded only a trace of residue, which crystallized on seeding with the starting material. The crude semicarbazone, when recrystallized from methanol, melted at 202–203°. The yield was 1.7 g.

The fractions (b.p. 100–110° and 140–160°) obtained on distillation of the noncrystalline products of the reaction of lead tetraacetate with 1-phenyl-1,2-butadiene also yielded the semicarbazone just described.

One and one-tenth grams of the distillate (b.p. 100–110°) was boiled for 7 hours with 1.2 g. of potassium acetate in 10 cc. of 90% ethanol, and the reaction-mixture, when treated as just described for the preparation of the semicarbazone, yielded 0.22 g., m.p. 203–205°.

Two grams of the fraction boiling at 140–160° treated in the same manner yielded 0.4 g. of the same semicarbazone.

Hydrolysis of ketone semicarbazone to 1-phenyl-3-methylcyclopropane-2-one (VI). Six-tenths gram of the semicarbazone was suspended in 10 cc. of water containing 1.2 g. of oxalic acid in a flask equipped for steam distillation, and a rapid current of steam was passed through the suspension. When the reaction was complete, as shown by the disappearance of the solid material, the combined distillates from three reactions were extracted with ether, the solution was dried, and the solvent removed. The residue on distillation yielded 1.0 g. of yellow liquid, b.p. 110–111° (10 mm.).

Anal. Calc'd for $C_{10}H_{10}O$: C, 82.14; H, 6.85.
Found: C, 80.67; H, 6.73.

The 2,4-dinitrophenylhydrazone was prepared by dissolving 0.1 g. of the compound in 10 cc. of ethanol containing 0.12 g. of 2,4-dinitrophenylhydrazine and adding a few drops of concentrated hydrochloric acid in a little ethanol to the boiling solution. The hydrazone separated at once and was removed by filtration. It melted at 201–202°; yield, 0.16 g.

Anal. Calc'd for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.29.
Found: C, 58.52; H, 4.16.

Hydrogenation of the ketone. When the ketone was shaken in the presence of platinum oxide catalyst in a hydrogen atmosphere in the usual manner, the reaction was very slow. After 1.5 hours, 0.45 g. absorbed 80 cc., or about 1 equivalent, of hydrogen. The reaction-product, which was isolated by dilution of the ethanol solution with water and extraction with ether, weighed 0.5 g. The material, however, was a mixture containing about 50% of unchanged ketone. Two-tenths gram of the reaction-product yielded 0.11 g. of semicarbazone by the usual procedure, which after recrystallization from ethanol melted at 205–206°, and was identified by the mixture melting point (204–205°) as the semicarbazone of the original ketone.

Two-tenths gram of the material yielded 0.15 g. of 2,4-dinitrophenylhydrazone, which after one recrystallization from ethanol melted at 198–200° and was identified by the mixture melting point (201–202°) as the 2,4-dinitrophenylhydrazone of the original ketone.

Permanganate oxidation of the ketone. One and three-tenths grams of the ketone was suspended in 130 cc. of water, and 4.5 g. of potassium permanganate was added in several portions to the rapidly stirred suspension at room temperature. Finally, the reaction-mixture was boiled for a few minutes and the manganese dioxide was removed by filtration. A slight excess of permanganate in the filtrate was decomposed with a little oxalic acid and the alkaline solution filtered clear. It was then concentrated to 15–20 cc. under reduced pressure. On addition of dilute sulfuric acid, a voluminous precipitate was obtained, which was removed and recrystallized from water. The yield was 0.8 g. The product melted at 122–123°, and a mixture of it with benzoic acid also melted at the same temperature.

Anal. Calc'd for $C_7H_6O_2$: Mol. wt., 122.
Found: Equiv. wt. (titration), 128.

The filtrate from the benzoic acid was distilled with steam, and the 150 cc. of distillate was neutralized with potassium hydroxide and evaporated to dryness. The dry salt weighed 0.9 g. Four-tenths gram of the salt, when boiled with 1.2 g. of *p*-toluidine and 0.4 g. of concentrated hydrochloric acid, furnished 0.2 g. of a product that was identified as acetyl-*p*-toluidide by the mixture melting point with authentic material (148°).

Reaction of lead tetraacetate with 1-cyclohexyl-2,3-pentadiene. Seven and five-tenths grams of 1-cyclohexyl-2,3-pentadiene (4) in 25 cc. of glacial acetic acid was warmed with 23 g. of lead tetraacetate for four hours with constant stirring, after which time the reagent was consumed. The acetic acid solution was treated according to method B by mixing with 150 cc. of absolute ether, filtering after the lead acetate had crystallized, and removing the solvents under reduced pressure. The residue was dissolved in ether, which was extracted with a small quantity of water, and then with dilute sodium bicarbonate solution. The dried solution was evaporated, leaving 10.4 g. of liquid residue. On distillation at 0.7 mm., 3.5 g. of the unchanged 1-cyclohexylpentadiene was recovered, b.p. 78–82°. This was followed by an intermediate fraction of 2.3 g. boiling at 82–90° and a third fraction of 2.0 g. boiling at 90–150°.

According to its acetyl content, the third fraction consisted largely of the diacetoxy addition-product.

Anal. Calc'd for $C_{15}H_{24}O_4$: 2 CH_3CO, 32.1. Found: CH_3CO, 29.9.

Saponification of the fraction boiling at 90–150°. The distillate was boiled for 4 hours with 15 cc. of 90% ethanol and 2 g. of potassium acetate. The reaction-product was isolated by dilution with water, extraction with ether, and washing the ethereal solution with water to remove the ethanol. On evaporation of the dried solution an oily residue was obtained, which reduced Fehling's solution strongly. On distillation it yielded 1.3 g. of material boiling at 80–120° (0.7 mm.).

p-*Nitrophenylosazone.* Two-tenths gram of the distillate in 5 cc. of ethanol was boiled for a few minutes with 0.3 g. of *p*-nitrophenylhydrazine hydrochloride, yielding 0.1 g. of red crystals, which were almost insoluble in the usual solvents. When recrystallized from nitrobenzene, this material melted at 278° after shrinking at 270°. The analysis indicates that it is the osazone derived from cyclohexylhydroxypentanone.

Anal. Calc'd for $C_{23}H_{28}N_6O_4$: C, 61.06; H, 6.20.
Found: C, 60.92; H, 6.01.

No crystalline semicarbazone was obtained from another portion of the product.

Reaction of lead tetraacetate with 2,3-pentadiene. A solution of 6 g. of 2,3-pentadiene (5) in 40 cc. of acetic acid was placed in a closed flask equipped with stirring mechanism and reflux condenser, 40 g. of lead tetraacetate added, and the suspension agitated at 35–40° for 4 hours or until the reagent had been used up. The reaction-product was isolated by method B. The distilled acetic acid was bright yellow and contained volatile reaction-products which were not isolated. The residue was freed from traces of lead acetate and acetic acid by the process already described, and then distilled and divided into 0.75 g. of fraction I, b.p. 55–80° (7 mm.), and 1.58 g. of fraction II, b.p. 80–105° (7 mm.).

Anal. Calc'd for $C_9H_{14}O_4$: 2 CH_3CO, 46.2.
Found: CH_3CO, fraction I, 36.7; fraction II, 44.3.

The higher-boiling fraction was boiled for 4 hours in 15 cc. of 90% ethanol containing 1.8 g. of potassium acetate. Three cubic centimeters of the resulting solution was boiled with about the same volume of a saturated ethanol solution of 2,4-dinitrophenylhydrazine containing a little hydrochloric acid. The separated crystalline product, when recrystallized from a large volume of acetic acid, melted at 283°. The analysis indicated it to be the 2,4-dinitrophenylosazone derived from a hydroxypentanone.

Anal. Calc'd for $C_{17}H_{16}N_8O_8$: C, 44.33; H, 3.48.
Found: C, 44.57; H, 3.56.

The remainder of the solution, when treated with semicarbazide hydrochloride and pyridine, yielded a small quantity of crystalline product of melting point 258–260°, which was identical with the disemicarbazone obtained in the following experiment.

The reaction of lead tetraacetate with 2,3-pentadiene was repeated, and 1.3 g. of the fraction of the reaction-product corresponding to the above fraction II was saponified by boiling for 2 hours with 10 cc. of ethanol containing 1 cc. of concentrated hydrochloric acid and 1 cc. of water. The yellow solution was distilled at atmospheric pressure and 9 cc. of distillate collected. Three cubic centimeters of the distillate, when mixed with an aqueous solution of 0.35 g. of *p*-nitrophenylhydrazine, gave an orange crystalline reaction-product, which was removed by filtration and washed with ethanol. It was almost insoluble in the usual reagents, but when recrystallized from nitrobenzene it melted at 285° after softening at 270°. The analysis indicates that it is probably the osazone derived from a hydroxypentanone.

Anal. Calc'd for $C_{17}H_{18}N_6O_4$: C, 55.13; H, 4.86.
Found: C, 57.64; H, 5.16.

Another aliquot of 3 cc. of the distillate, on treatment with semicarbazide hydrochloride, furnished a crystalline derivative, almost insoluble in the usual solvents, and melting at 257–258°. The analysis agreed for the disemicarbazone of a pentandione.

Anal. Calc'd for $C_7H_{14}N_6O_2$: C, 39.25; H, 6.54.
Found: C, 39.74; H, 6.59.

The compound was identical with the disemicarbazone obtained by potassium acetate hydrolysis as shown by the mixture melting point (256–257°).

It seems likely, from the results obtained, that saponification of the diacetoxy compound by either method results in a mixture of *alpha*-hydroxy ketone and the *alpha*-diketone formed from it by oxidation. Both compounds would furnish an osazone and the latter a disemicarbazone.

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