Retene investigations

I. Acetyl retene

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Retene, 1-methyl-7-isopropyl phenanthrene, which occurs in considerable quantities in pine wood tar, has in later years attracted the attention of several chemists, not only with regard to its industrial possibilities but also because of its peculiar chemical properties.

The investigation of retene substitution products is complicated by the fact that a great number of isomers may be formed simultaneously and may be extremely difficult to separate because many retene derivatives are very slowly crystallizing substances or, while in mixture with closely related compounds, completely unable to crystallize.

The introduction of an acetyl group by means of the Friedel-Crafts reaction has been studied by several authors¹⁻⁴. All of them have used acetyl chloride in either carbon disulfide or nitrobenzene for the reaction. Nyman (*l. c.*) reports a total yield of 60 % without stating the amount of pure compound obtained. All the said investigators have isolated only one acetyl retene, *viz.* 3-acetyl retene, m. p. 99°, the yield of this compound varying but never exceeding 45 %.

In this laboratory acetic anhydride has been used instead of acetyl chloride. It hardly makes any difference as to the products obtained, but the low vapour pressure of the anhydride as compared with the acid chloride is a definite advantage. Various solvents have been used, in addition to the aforementioned: tetrachloro ethane and trichloro ethylene. The total yield of acetyl retenes is practically independent of the solvent chosen; but the yields of the different isomers vary considerably with the nature of the solvent, nitrobenzene being the most favorable for the formation of the 3-substitute.

In our experiments we, rather surprisingly, have found a new isomer which is less soluble and more readily crystallizing than 3-acetyl retene. The reason

why it has escaped the attention of the earlier workers may be that in carbon disulfide relatively small amounts are formed. Trichloro ethylene seems to be most favorable for the new compound. While only 5—8 % are formed in carbon disulfide and nitrobenzene some 15 % can be isolated from the reaction mixture when trichloro ethylene is used.

The new acetyl retene has m. p. 156—57° and is very slightly soluble in alcohol, ether, and glacial acetic acid, more soluble in benzene. The position of the acetyl group has been determined in the following way. The substance is oxidized with chromic acid in acetic acid to a quinone with the same melting point as an acetyl retene quinone which has been obtained by Nyman⁵ by oxidation of 2-acetyl-9,10-dihydroretene the constitution of which has been established by him. In order to secure the identity of these quinones the new one was oxidized with hydrogen peroxide and gave the same diphenic acid and its anhydride as those described by Nyman. The 2-position of the acetyl group is thus firmly established.

2-Acetyl retene

3-Acetyl retene

In a recent paper⁶ Buu-Hoi and co-workers claim to have isolated a diacetyl retene, m. p. 157°, by direct acetylation of retene in carbon disulfide, and to have prepared 2-acetyl retene, m. p. 151°, by dehydrogenation of 2-acetyl dihydroretene with selenium. They state that the latter is very soluble in hot alcohol which, however, is not the case with our compound. There can hardly be any doubt about the identity of their 'diacetyl retene' with our 2-acetyl retene. As we have prepared and analyzed several derivatives of this substance we believe that an analytical error has misled the French authors. The purpose of their experiment: to prove that 2-substitution can occur in retene, is, however, fulfilled through our results.

When 2- and 3-acetyl retenes are removed in crystalline form from the reaction mixture (see experimental part) the remaining oil is distilled under reduced pressure and a very viscous light yellow oil is obtained from which no crystalline material has hitherto been isolated. Practically the entire distillate passes over within 2—3 degrees when heating and pressure are kept constant. It is, therefore, hopeless to attempt a separation of the components through fractional distillation.

The mixture still contains some 2- and 3-acetyl retene, but the bulk of the oil consists of two or more hitherto unknown acetyl retenes which have with-

stood all efforts of isolation. The content of 3-acetyl retene can be estimated by addition of dinitrophenyl hydrazine to a hot solution of the oil in glacial acetic acid, the dinitrophenyl hydrazone of 3-acetyl retene being nearly insoluble in the said solvent while the other hydrazones are rather soluble. 2-Acetyl retene reveals its presence when the oil is oxidized with sodium hypochlorite. Of the resulting retene carboxylic acids — which are being investigated at present and shall be dealt with in another paper — the 2-acid forms an extremely slightly soluble sodium salt crystallizing out in the oxidation mixture.

Attempts to isolate the unknown acetyl retenes as picrates have been unsuccessful, these picrates being very soluble in alcohol, benzene, and ether at room temperature. On cooling an alcoholic solution of the picrates to 0° or below a yellow oil separates which on long standing solidifies, but at room temperature the mass liquefies completely again and so far no solvent has been found by means of which a fractional crystallization has been possible.

Separation through phenyl hydrazones, too, has been tried in vain.

A number of derivatives of 2-acetyl retene are described.

EXPERIMENTAL PART

1. Preparation of acetyl retenes

Retene * (0.5 mole, 120 g), dissolved in trichloro ethylene (500 ml), and acetic anhydride (0.55 mole, 56 g) are placed in a flask provided with an efficient stirrer and cooled with running water. In the course of 30–40 minutes finely powdered aluminium chloride (1 mole, 135 g) is added in 7–8 portions and stirring is continued for 2–3 hours. In some instances the aluminium chloride-ketone complexes formed crystallize out suddenly making stirring temporarily inefficient. By means of a spatula the paste formed is broken and becomes again mobile.

The product is decomposed with ice and hydrochloric acid and the light yellow solution is separated, washed with water, and dried with calcium chloride. The solvent is removed by distillation from a water bath at reduced pressure. The remaining oil is cooled and diluted with ether (300 ml). On short standing — sometimes immediately — a crystallization sets in and after 2–3 hours at room temperature the crystals are filtered off with suction and washed with ether. The crystalline product is almost pure 2-acetyl retene the yield of which is about 15 g. It may be recrystallized from a large volume of alcohol or from glacial acetic acid.

The filtrate from 2-acetyl retene then is placed in a refrigerator at 0° for 24 hours when a few grams (3–5) of 3-acetyl retene have separated and are filtered off. Concentration of the filtrate and renewed standing at 0° in 2 days may yield another small

* Thanks are due to Dr. K. J. Karrman, Lund, Sweden, who has kindly supplied the crude retene used in this investigation. The product was distilled under reduced pressure (0.5–1 mm) before use, m. p. 95–96°.

amount of 3-acetyl retene. The rather viscous mother liquor is freed from ether and trichloro ethylene by heating on the steam bath and suction with the water pump and is then distilled at 0.1–0.2 mm mercury. When the heating and the pressure is kept as constant as possible the distillation proceeds at practically constant temperature (about 190°) during nearly the entire distillation. Toward the end the temperature of the bath is raised some twenty degrees. In the flask a dark mass remains which solidifies on cooling but yields no crystalline products. It is soluble in benzene and in trichloro ethylene and consists probably mainly of diacetyl retenes. — Total yield of crystallized and distilled acetyl retenes 110–120 g. An elementary analysis of the distilled oil — which is very viscous at room temperature — shows it to be a mixture of pure monoacetyl retenes. It has a light yellow colour.

When tetrachloro ethane is used as a solvent it is removed (after decomposition of the aluminium chloride complex) by steam distillation. When the tough ketone mixture is taken up in ether the 2-acetyl compound usually crystallizes out immediately. The yield of this substance is somewhat lower than from trichloro ethylene while a higher yield of 3-acetyl retene is obtained.

2. 2-Acetyl retene. $C_{18}H_{17}COCH_3$

Recrystallized from alcohol or glacial acetic acid the new compound melts at 156–57°. Slightly soluble in all common solvents at room temperature. It dissolves in conc. sulphuric acid with an orange-yellow colour very similar to that of 3-acetyl retene in the same solvent. (comp. the corresponding cinnamalaceto retenes below).

$C_{20}H_{20}O$	Found	C 86.9	H 6.99
	Calc.	» 86.95	» 7.25

a. *Semicarbazone*, from alcohol, m. p. 264–68° (decomposition).

$C_{21}H_{24}ON_3$	Found N 12.46	Calc. N 12.57
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b. *Oxime* 'from alcohol' m. p. 214–17° with decomp.

$C_{20}H_{21}ON$	Found N 4.81	Calc. N 4.80
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c. *Phenylhydrazone*. To a hot solution of 2-acetyl retene (1 g) in glacial acetic acid (15 ml) is added phenyl hydrazine (0.6 g) in 50 % acetic acid (2 ml) and the mixture is boiled for 10 minutes. On cooling, the phenyl hydrazone separates as an oil which on scratching soon solidifies. Recrystallized from 90 % acetic acid or from alcohol it melts at 119°.

$C_{26}H_{26}N_2$	Found N 7.17	Calc. N 7.10
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d. *Dinitrophenyl hydrazone*. On boiling a solution of equimolar amounts of the ketone and dinitrophenyl hydrazine in glacial acetic acid for ten minutes and cooling, the dinitrophenyl hydrazone crystallizes out, m. p. after recrystallization from acetic acid 176–77°.

$C_{26}H_{24}O_4N_4$	Found N 12.5	Calc. N 12.3
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The isomeric *3-acetyl retene dinitrophenyl hydrazone* has not been described before. It is rapidly formed when the two reactants are brought together in boiling glacial acetic acid solutions. It is very sparingly soluble in acetic acid, very much more so than the corresponding derivatives of the other acetyl retenes. It is peculiar that its m. p. (297–99°) is 100° higher than that of the 2-isomer while the ketone proper melts considerably lower (at 99°) than the 2-ketone. As mentioned in the theoretical part, the precipitation of 3-acetyl retene dinitrophenyl hydrazone on treatment of the distilled ketone mixture with dinitrophenyl hydrazine shows the presence of the 3-isomer in the mixture and by weighing the precipitate the content of this compound was found to be 20–30 %.

$C_{26}H_{24}O_4N_4$ Found N 12.35 Calc. N 12.3

e. *2-Acetyl retene quinone*. 2-Acetyl retene (2 g) is dissolved in hot glacial acetic acid (30 ml). At about 70° a solution of chromic acid anhydride (3 g) in water (5 ml) is added dropwise with shaking. After 10 minutes at 70° water (10 ml) is added. On cooling, the quinone separates, is filtered off, washed with dilute acetic acid and recrystallized from 90 % acetic acid. Very beautiful orange red crystals which are very sensitive to light. M. p. 197–98°.

$C_{20}H_{18}O_3$ Found C 78.0 H 5.88
Calc. » 78.4 » 5.93

The quinone was oxidized with hydrogen peroxide in glacial acetic acid as described by Nyman⁵. The same 3-methyl-4'-isopropyl-4-acetyl diphenic acid, m. p. 207°, and its anhydride, m. p. 155°, were obtained.

3. Retene-2-carboxylic acid. $C_{18}H_{17}COOH$

2-Acetyl retene (0.01 mole, 2.76 g) is dissolved in dioxane (20 ml) and heated to 95°. Sodium hypochlorite (about 50 % excess), made from sodium hydroxide and chlorine in the usual manner and titrated, is slowly added with efficient stirring while the temperature is kept between 90 and 100°. The slightly soluble sodium salt of the acid crystallizes out during the reaction. After cooling the mixture the salt is filtered with suction and washed with cold water. It is boiled with about 700 ml water to which is added a little ammonia, filtered from a small amount of unchanged acetyl retene and acidified with hydrochloric acid. The dried product is recrystallized from xylene. M. p. 275–78° after sintering at about 260°. It sublimes noticeably at the melting point.

$C_{18}H_{18}O_2$ Found C 81.8 H 6.40
Calc. » 82.0 » 6.47

4. 2-Cinnamoyl retene (benzalaceto retene). $C_{18}H_{17}COCH:CHC_6H_5$

2-Acetyl retene (2 g) is dissolved in boiling alcohol (200 ml), benzaldehyde (1 g) is added and the solution is cooled with shaking to about 60° when the acetyl retene has partly separated in small crystals. Then a solution of potassium hydroxide (1 g) in alcohol (10 ml) is added and the mixture shaken with hand. The crystals soon disappear whereupon the condensation product begins to crystallize in beautiful light yellow plates. After

standing half an hour the crystals are filtered off and recrystallized from alcohol. M. p. 147–48°.

$C_{27}H_{24}O$	Found	C	89.2	H	6.64
	Calc.	»	89.0	»	6.64

Similarly *2-cinnamalaceto retene*, $C_{18}H_{17}COCH:CHCH:CHC_6H_5$ is formed by condensation of cinnamic aldehyde with 2-acetyl retene. Yellow crystals from benzene, m. p. 189°. Yield almost quantitative.

$C_{29}H_{26}O$	Found	C	89.7	H	6.71
	Calc.	»	89.2	»	6.67

2-Cinnamalaceto retene dissolves in conc. sulphuric acid with a pure red colour while the halochromic colour of the isomer 3-compound resembles the colour of a permanganate solution.

5. 2-(α -Hydroxyethyl)-retene. $C_{18}H_{17}CHOHCH_3$

2-Acetyl retene (5.8 g) is reduced with aluminium-isopropoxide (40 ml of a molar solution in isopropyl alcohol + 60 ml isopropyl alcohol) in the usual manner⁷. The reduction is complete in about 90 minutes. An excess of cold dilute hydrochloric acid is added with stirring to the cooled reaction mixture. The precipitate is filtered off and washed with dilute alcohol. Yield almost quantitative. Recrystallized from alcohol the compound melts at 171–73°.

$C_{20}H_{22}O$	Found	C	85.9	H	8.05
	Calc.	»	86.3	»	7.95

6. 3-(α -Hydroxyethyl)-retene. $C_{18}H_{17}CHOHCH_3$

This compound is made from 3-acetyl retene in the same way. On addition of hydrochloric acid to the reaction mixture the carbinol separates as an oil which soon solidifies. This carbinol is considerably more soluble and more slowly crystallizing than the 2-isomer. Yield nearly quantitative. Recrystallized from alcohol its m. p. is 115–116°.

$C_{20}H_{22}O$	Found	C	86.0	H	7.93
	Calc.	»	86.3	»	7.95

SUMMARY

Introduction of an acetyl group into retene by means of the Friedel-Crafts reaction leads to a number of isomers. In addition to the previously known 3-acetyl retene a new isomer has been isolated and identified as 2-acetyl retene, but at least two other isomers are formed in considerable amounts. The relative amounts of the different components of the reaction product depend upon the solvent chosen for the reaction. Trichloro ethylene is shown to be an excellent solvent for the Friedel-Crafts reaction.

A number of compounds prepared from 2- and 3-acetyl retene are described: besides some functional derivatives, retene-2-carboxylic acid and the two secondary alcohols corresponding to the ketones.

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