TABLE I

EFFECT OF INORGANIC SALTS ON RICINUS LIPASE ACTION

In each experiment, 1.00 g. olive oil, 0.050 g. lipase preparation (L. U. = 910) and 0.6 ml. of 0.1 N acetic acid containing 100 mg. of the salts indicated were shaken together for three minutes at the start, then let stand at 37–38°.

Salt added	Time of digestion, min. 20	25	40
None (check)	38.8	43.6	53.0
Mercuric acetate	1.2	2.0	2.1
Mercuric chloride	2.6	2.7	2.6
Cupric acetate	4.0	4.1	4.1
Cobalt acetate	10.4	12.0	13.0
Ferric chloride	9.9	10.3	15.5
Zinc chloride	9.6	20.0	23.2
Lead acetate	18.0	20.7	28.0
Lead chloride	21.0	24.0	31.4
Mercurous chloride	22.9	28.1	35.0
Chromium chloride	26.2	27.5	28.5
Nickel chloride	26.9	30.4	38.1
Calcium acetate	28.6	33.9	42.8
Manganese acetate	27.9	33.4	44.8
Manganese chloride	28.5	32.0	40.0
Ferric acetate	32.0	37.6	53.4
Chromium acetate	35.9	42.8	53.0

tion was not so marked in these cases). It is interesting to note that the preparations at this Laboratory invariably contain 7.15–7.25% ash which on qualitative analysis has been shown to contain manganese, magnesium, calcium and iron.[23] These naturally occurring salts have not shown any marked effect on the lipase action except when added in fairly high concentration. These observations support the findings of Willstätter and Waldschmidt-Leitz[11] that manganous salts had no stimulating effect under optimum conditions of activity.

While optimum conditions were maintained in the experiments with cholesterol, a preparation with a lower lipase unitage (L. U. = 285) was used.[24] In this way, cholesterol was shown to have a definite stimulating effect on the rate of Ricinus lipase action. The effect is the more pronounced in the early stages of the hydrolysis, complicating factors[24] probably accounting for the same extent of hydrolysis being reached in each of the three series. It is suggested that this stimulation was due to the formation of a desirable emulsion, water-in-oil. In a separate series of unreported experiments, the effects of other substances chiefly gums known to produce definite types of emulsions were studied. Abnormally low figures were obtained for the percentage hydrolysis in these cases. It is quite possible that these results were due to the emulsifying agents. This problem is receiving further study.

Summary

The effect of certain salts, chiefly chlorides and acetates, on the activity of Ricinus lipase has been studied. Each added salt retarded or inhibited the normal action of the enzyme. Salts of cobalt, copper and mercury showed the greatest inhibiting action. Iron, lead, nickel and zinc salts definitely retarded the action, as to a less extent did the salts of calcium, chromium, and manganese.

Cholesterol has been shown to accelerate the action of Ricinus lipase. This observation is taken to indicate further that a water-in-oil emulsion is desirable for Ricinus lipase action.

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[23] We are indebted to Mr. W. H. Stahl for these analyses.

[24] Longenecker and Haley, THIS JOURNAL, **59**, 2156 (1937).

STATE COLLEGE, PENNA. RECEIVED JULY 16, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

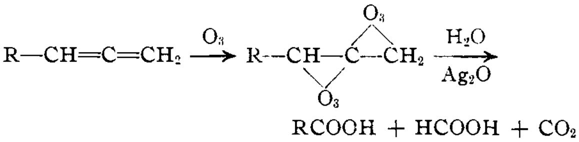
The Rearrangement of Acetylenes into Allenes at High Temperature

BY CHARLES D. HURD AND ROBERT E. CHRIST

This paper deals especially with the pyrolysis of 1-hexyne and 1-heptyne by the flow method. The moles of gas produced per mole of hexyne decomposed at 500 and 600° were 0.34 and 1.03, respectively. These ratios for heptyne were 0.83 and 2.0. The chief gaseous products in all experiments were propylene, methane and ethylene. Lesser quantities of ethane and hydrogen were observed but no more than a trace of acetylene was ever found among the products.

The liquid products were distilled through a very sensitive fractionating column and the various fractions were studied. The important reaction products found were 1,2-hexadiene (propylallene) from 1-hexyne, and 1,2-heptadiene (butylallene) from 1-heptyne. Traces of 2-hexyne or 2-heptyne were evident in the experiments at 600°, but not otherwise. Conjugated hydrocarbons were absent and no evidence could be obtained for benzene or toluene among the products. The liquids from heptyne yielded small quantities of pentenes and hexenes.

To prove the presence of the allenes the fraction in question was freed from its 1-alkyne content by precipitation as the silver salt. The remaining liquid was subjected to ozonolysis. From 1,2-hexadiene there was obtained a mixture of butyric and formic acids, and from 1,2-heptadiene a mixture of valeric and formic acids. If 2-hexyne or 2-heptyne had been present, acetic acid would have been formed also on ozonolysis. No more than a trace of acetic acid was ever found and usually it was absent. Hence, significant amounts of 2-alkynes could not have been present.

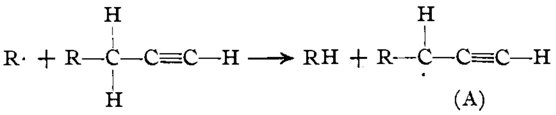


$$R-CH=C=CH_2 \xrightarrow{O_3} R-\underset{O_3}{CH-\overset{O_3}{C}}-CH_2 \xrightarrow[Ag_2O]{H_2O} RCOOH + HCOOH + CO_2$$

The pyrolysis of hexyne has never been studied previously but 1-heptyne has received attention. The first to study it was Guest[1] who noted isomerization of 1-heptyne when it was passed over pumice at 350°. He assumed that the isomers were acetylenic, *i. e.*, either 2- or 3-hexyne, and made no reference to 1,2-heptadiene. A more recent investigation is that of Bachman and Hill,[2] who found that in a sealed tube with soda-lime it was unaffected if heated for one hour at 275° but that it was completely polymerized in one hour at 300°.

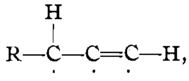
The evidence regarding the pyrolysis of 1-alkynes may be summarized as follows. At moderate temperatures, polymerization sets in at a rate which must increase with the temperature. At significantly higher threshold temperatures, however, two other effects are noted: (1) partial decomposition into simpler products, (2) partial isomerization into 1,2-alkadienes. It is noteworthy that the temperature required for the isomerization is about the same as that required for the decomposition into gases.

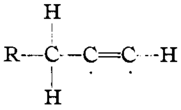
To account for the reactions which are noted at the higher temperatures, it may be assumed that radicals (R·) are formed which initiate a chain mechanism, as follows



$$R\cdot + R-\overset{H}{\underset{H}{C}}-C\equiv C-H \longrightarrow RH + R-\overset{H}{\underset{\cdot}{C}}-C\equiv C-H$$

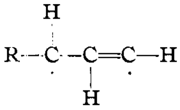
(A)

Radical A should be regarded as tervalent,  $R-\overset{H}{\underset{\cdot}{C}}-\underset{\cdot}{C}=\underset{\cdot}{C}-H$, instead of univalent, because of the high temperature involved. In perpetuating the chain reaction this radical may appropriate hydrogen from a neighboring molecule in one of three ways to yield B, C or D.



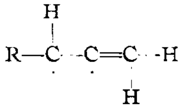
$R-\overset{H}{\underset{H}{C}}-\underset{\cdot}{C}=\underset{\cdot}{C}-H$

(B)



$R-\overset{H}{\underset{\cdot}{C}}-\underset{H}{C}=\underset{\cdot}{C}-H$

(C)



$R-\overset{H}{\underset{\cdot}{C}}-\underset{\cdot}{C}=\underset{H}{C}-H$

(D)

All three of these radicals may polymerize, but this effect should be particularly evident with C. Most of B should yield the original acetylene, thereby diminishing the apparent extent of decomposition. D would escape from the reaction zone as an allene, $RCH=C=CH_2$. As noted above, the presence of allenes was established definitely. This conclusion was strongly suspected, but not definitely established in earlier work[3] with 1-propyne and 1-butyne.

Since a delicate method of analysis for 1,3-butadiene has become available recently, an experiment with 1-butyne was carried out at 560° to test for this conjugated hydrocarbon among the reaction products. None of it was detected.

Experimental Part

Materials.—The details of the synthesis of 1-hexyne and 1-heptyne, and the purification by way of the silver salt have been recorded:[4] 1-hexyne, b. p. 71°, $n^{19}_{\rm D}$ 1.400; 1-heptyne, b. p. 98.5°, $n^{20}_{\rm D}$ 1.417. 1-Butyne was prepared by the method of Hurd and Meinert.[5]

Apparatus and Procedure.—The apparatus was similar to that used during the pyrolysis of the pentenes.[6] The furnace was 75 cm. long and the reaction tube (1.6 cm. i. d.) had an effective hot volume of 117 cc. The hexyne or heptyne was introduced at a uniform rate into the top of the reaction tube by mercury displacement and liquids were condensed from the effluent gas by two traps connected in series at 0° and at −80°. The uncondensed gas was stored in a gas receiver. At the end of the run these traps were allowed to come to room temperature and the gas which escaped was taken to the gas receiver.

The gas was analyzed by liquefaction and distillation from an analytical column of the Podbielniak type combined with the usual absorption–combustion analysis.

A special column was constructed for precise distillation of the liquid products of the reaction. Its efficiency was high since it consisted of a vacuum-jacketed tube 36 cm. long and 5 mm. in diameter packed with a coil of No. 21 monel wire which had seven turns per cm. The jacket was evacuated by a set of double-stage mercury pumps. At the bottom end, the column was adapted to a 200-cc. flask by a ground glass joint. Very little liquid was held up in this column. The best fractionation was obtained by regulating the heat so that the wire coil was barely wet. Ordinarily, one to three hours was required for the distillation of a 10–15 cc. sample. A similar but smaller apparatus (16-cm. column, attached to a 45-cc. flask) was also used in some of this work.

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(1) Guest, THIS JOURNAL, **50**, 1746 (1928).

(2) Bachman and Hill, *ibid.*, **56**, 2730 (1934).

(3) Meinert and Hurd, *ibid.*, **52**, 4549 (1930); Hurd and Meinert, *ibid.*, **53**, 292 (1931).

(4) Hurd and Christ, *J. Org. Chem.*, **1**, 143 (1936).

(5) Hurd and Meinert, THIS JOURNAL, **53**, 296 (1931).

(6) Hurd, Goodyear and Goldsby, *ibid.*, **58**, 236 (1936).

TABLE I

PYROLYSIS OF 1-HEXYNE AND 1-HEPTYNE

Temp., °C.	Time., sec.	Press., mm.	1-Alkyne Taken, g.	1-Alkyne Not recovered g.	1-Alkyne Not recovered mole (X)	Liq. recov., g.	Exit gas liters	Exit gas mole (Y)	Total dec., %	$Y \div X$	Compn. exit gas, % by vol. Acetylenes	C_3H_6	C_2H_4	CH_4	C_2H_6	H_2
							1-Hexyne									
500	20.3	744	18.00	5.31	0.0648	17.08	0.48	0.0214	29.5	0.34	...	32.4	22.5	39.4	4.2	1.4
550	16.6	748	18.00	12.32	.1507	15.58	2.40	.107	68.6	.71	0.4	34.4	22.4	30.8	4.6	7.5
600	14.2	759	18.00	17.7	.2158	11.24	5.00	.223	98.2	1.03	1.0	33.8	23.6	22.0	10.4	9.2
							1-Heptyne									
500	22.5	746	20.0	7.20	.075	18.6	1.40	.0625	36	0.83	...	23.8	32.6	35.5	8.2	..
550	19.1	748	17.6	9.86	.1025	15.1	1.95	.0872	56	.85	...	26.2	30.6	26.7	9.7	6.8
600[a]	13.2	746	20.0	19.6	.2042	10.2	9.00	.402	98	2.0	...	26.9	25.6	28.4	8.2	7.9

[a] The exit gas in this run also contained butane, 0.4%; butylenes, 2.6%.

Pyrolysis of 1-Hexyne and 1-Heptyne

The 1-hexyne, purified through the silver salt was studied at 500, 550 and 600°, experiment having shown that little or no decomposition occurs in fourteen seconds at 400°. 1-Heptyne was studied at 500–600° with the same apparatus and methods. The data for both compounds are collected in Table I.

Analysis of Liquid Products

For each temperature the 1-hexyne or 1-heptyne content of the recovered liquid was determined quantitatively by Hill and Tyson's method[7] in which 0.2–0.3 g. samples are shaken with 10 cc. of 5% alcoholic silver nitrate solution. After six hours the precipitate is filtered off on a Gooch crucible, the excess silver precipitated with sodium chloride and the nitric acid titrated with standard sodium hydroxide. In duplicate analyses the content of 1-hexyne was found to be 74.3 ± 0.55% at 500°, 36.15 ± 0.15% at 550°, and 2.9 ± 0.1% at 600°, while for 1-heptyne the results were 68.7 ± 0.1% at 500°, 51.5% at 550°, and 2.55 ± 0.05% at 600°. For each experiment the remainder of the liquid was fractionated through the special column, and the results of these are given below in detail.

1-Hexyne

500°-Experiment.—The 16.5 g. of material, $n^{18.5}\mathrm{D}$ 1.407, was separated into five 4-cc. fractions (total weight, 15.4 g.), each boiling at 70–71°, and each having the same index of refraction, $n^{18.5}\mathrm{D}$ 1.400. The residue, $n^{18.5}\mathrm{D}$ 1.512, weighed 1.02 g. It was subjected to ozonolysis since it would contain the bulk of the 1,2-hexadiene (b. p. 78–79°, $n^{17}\mathrm{D}$ 1.430), 2-hexyne (b. p. 83–84°, $n^{21}\mathrm{D}$ 1.414), or the polymers.

The residue was freed from 1-hexyne by treatment with a mixture of silver nitrate, carbon tetrachloride and enough water to dissolve the silver nitrate. (Alcohol, as solvent, was avoided here because of the subsequent ozonolysis.) The pearl-white precipitate was filtered off and the filtrate was distilled from the excess of silver nitrate. The distillate of carbon tetrachloride and hydrocarbons was dried and subjected to ozonolysis. This method of removing the 1-hexyne or 1-heptyne from the fractions to be ozonized was used in all subsequent experiments.

A slow stream of ozonized oxygen (65 liters of 5% O_3) was passed through the solution at 0° for twenty-three hours. To decompose the ozonide, the mixture was warmed on the steam-bath with an equal volume of water, treated with freshly prepared silver oxide to convert aldehydes to acids, and then distilled. The volatile acids were neutralized with 68.00 cc. of 0.1035 *N* sodium hydroxide solution and the mixture was evaporated to dryness. There was 0.0025 mole of sodium formate in the residue, for it required 80.9 cc. of 0.0210 molar potassium permanganate solution to oxidize it. The solution was then acidified with sulfuric acid and distilled. A total of 0.0027 mole of butyric acid was found in the distillate (≈ 26.40 cc. of 0.1035 *N* sodium hydroxide). After neutralization and evaporation, 0.30 g. of sodium butyrate was obtained. It was caused to react with 0.30 g. of *p*-bromophenacyl bromide to yield *p*-bromophenacyl butyrate, m. p. 60°. A mixed m. p. determination with material of known purity, m. p. 62–63°, was 60–61°. This is evidence for 1,2-hexadiene, but not 2-hexyne.

550°-Experiment.—Fifteen grams of liquid was subjected to fractionation on the special column (g., °C., $n^{18.5}\mathrm{D}$): 3.8, 68.5–70, 1.4030; 3.8, 70–71, 1.4045; 3.7, 71–72.5, 1.4045. At this point, the residual liquid underwent a spontaneous, exothermic reaction (violent ebullition), turning color to an intense red. The polymer (3.3 g.) was non-volatile up to 150°. It absorbed bromine readily, was non-reactive toward alcoholic silver nitrate, and ozonolysis of a gram of it yielded a mixture of formic and acetic acids in about the ratio of four to one.

The fractions of distillate were combined, the 1-hexyne removed as before, and the remaining hydrocarbons analyzed by the method of ozonolysis and subsequent oxidation outlined above. The total acids were equivalent to 210.0 cc. of 0.1035 *N* alkali. The formic acid content represented 0.0114 mole (≈ 361.0 cc. of 0.0210 *M* potassium permanganate).

The solution was then acidified with sulfuric acid and distilled. Duclaux values for the volatile acid (18.3, 15.6, 13.3) corresponded to those for butyric acid. The solution from the Duclaux determination was evaporated to obtain 0.87 g. of sodium butyrate which yielded 0.29 g. of *p*-bromophenacyl *n*-butyrate, m. p. 60–62° (mixed m. p. 60–61°).

600°-Experiment.—Fractionation of the liquids in the small special column gave these data (g., °C., $n^{18.5}\mathrm{D}$): 1.0, 68.5–72, 1.4238; 0.8, 72–80, 1.4340; 0.8, 80–90, 1.4495; 0.9, 90–115, 1.4708; 3.9, residue, 1.5750. The first two fractions were combined, freed from 1-hexyne,

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(7) Hill and Tyson, THIS JOURNAL **50**, 172 (1928).

and the hydrocarbons (in carbon tetrachloride) were ozonized. The ozonide was decomposed with water. This treatment alone sufficed to convert most of the formaldehyde into formic acid which, therefore, was neutralized and distilled. The residue of sodium formate was converted into *p*-bromophenacyl formate,[8] m. p. 140°. The distillate, composed of aldehydes, water and carbon tetrachloride, was refluxed for five hours with freshly prepared silver oxide. It was then acidified with sulfuric acid and distilled. The volatile acids required 82.2 cc. of 0.0980 *N* alkali for neutralization, and evaporation yielded 0.58 g. of salts. Reaction of the latter with *p*-bromophenacyl bromide yielded the butyrate which melted at 60° after several crystallizations.

The 80–90° fraction contained no more than a trace of 1-hexyne, which was removed in the usual manner. The rest was ozonized, hydrolyzed with water, distilled and the acids neutralized with 92.3 cc. of 0.1035 *N* alkali. The carbon tetrachloride was then distilled off and the remaining aqueous solution oxidized by 300 cc. of 0.0101 *M* potassium permanganate. In this process formic acid was destroyed. Duclaux values (13.4, 10.0, 9.3) of the remaining acids pointed to a mixture of butyric and acetic acids.

The 90–115° fraction was unsaturated toward bromine and did not contain conjugated double bonds, for it did not react appreciably with maleic anhydride.

About 2.5 g. of the 3.9 g. of residue was mixed with the similar 2.1 g. of unused residue from the 550° run. Distillation at 15 mm. caused the separation into two fractions, and left 1.6 g. of a black, tarry residue. The first fraction (80–100°, 1.44 g., n^{20}_D 1.5145) seemed to be a dimer, and the second fraction a trimer (185–200°, 1.64 g., n^{20}_D 1.5508).

1-Heptyne

500°-Experiment.—The entire 18 g. distilled between 97–98.5°. Its content of 1-heptyne was removed in the usual manner (by aqueous silver nitrate in the presence of carbon tetrachloride) and the remaining hydrocarbons (in carbon tetrachloride) were ozonized. After hydrolysis of the ozonide with water, the aldehydes present were oxidized to acids by refluxing the mixture with freshly prepared silver oxide. This treatment was followed by the usual acidification with sulfuric acid, distillation, removal of the formic acid with potassium permanganate solution, redistillation, neutralization and evaporation. The salt which remained, on reaction with *p*-bromophenacyl bromide, yielded 0.21 g. of *p*-bromophenacyl valerate, m. p. 57° (mixed m. p. 58°).

550°-Experiment.—The liquid was freed of its 1-heptyne content, ozonized and hydrolyzed with water. This process seemed to oxidize the formaldehyde more readily than the other aldehydes; therefore, the solution was neutralized with sodium hydroxide and distilled. The residual salt weighed 0.47 g. That it was sodium formate was evident by Duclaux values and by a derivative. The salt, treated with sulfuric acid and distilled, gave a solution of volatile acid whose Duclaux values (4.2, 4.5, 4.6, 5.1) were characteristic of formic acid. The recovered sodium formate, on treatment with *p*-bromophenacyl bromide, yielded *p*-bromophenacyl formate, m. p. 138°.

The other aldehydes which were distilled off with the solvent were oxidized by refluxing for three hours with freshly made silver oxide. The acid proved to be valeric for the Duclaux values, obtained as before, were 24, 20 and 13.

600°-Experiment.—Distillation of the liquid through the small special column gave these fractions (symbol, g., °C.): A, 0.05, 29–30; B, 0.19, 36–37; C, 0.15, 68–70; D, 2.74, 82–99; E, 1.62, 175–218; residue, 5.50.

From its boiling point, unsaturation toward bromine, and inertness toward alcoholic silver nitrate solution fraction A is regarded as 1-pentene. Similarly, B appeared to be 2-pentene. It was analyzed quantitatively with bromide–bromate according to the directions of Francis:[9] subs. 0.0903 g.; cc. of 0.5403 *N* bromide–bromate solution, 6.45; cc. of 0.1700 *N* thiosulfate solution to back-titrate, 4.48; bromine atoms absorbed per mole, 2.1 (calculated for C_5H_{10}, 2.0).

Judged by the distilling temperature, fraction C may have contained hexylenes, but the bromine number of 2.4 was somewhat high (subs. 0.1249 g.; cc. of 0.5403 *N* bromide–bromate, 7.35; cc. of 0.1700 *N* thiosulfate, 2.72). 1-Alkynes were not present in quantity sufficient to react with alcoholic silver nitrate solution.

Most of the recovered 1-heptyne was in fraction D. Analysis of the 2.74 g. showed it to contain 9.2% of 1-heptyne. To see whether benzene was present, 6 drops of it was heated half a minute with 1 cc. each of concd. sulfuric and fuming nitric acids. The mixture when poured into 10 cc. of water, yielded no dinitrobenzene.

The 1-heptyne was removed from the rest of D (about 1 cc.) and the mixture was ozonized. The ozonide was decomposed with water, the acids neutralized with sodium hydroxide, and the mixture evaporated. The solid residue, on reaction with *p*-bromophenacyl bromide, gave rise to *p*-bromophenacyl formate, m. p. 134°. The quantity was too small to purify adequately but when mixed with an authentic specimen (m. p. 140°) the fusion temperature was 136°.

Fractions E and F represented the same type of polymers as were noted in the work with hexyne. This material was a heavy, slightly-yellow oil with a pleasant odor. It was unsaturated but it formed no precipitate with alcoholic silver nitrate solution. It absorbed 1.5 g. of bromine per gram of substance: (subs. 0.2186 g.; cc. of 0.5403 *N* bromide–bromate solution, 8.00; cc. of 0.1700 *N* thiosulfate solution, 1.31).

Pyrolysis of 1-Butyne

A contact time of 11.2 sec. was maintained during the pyrolysis of 5000 cc. of 1-butyne gas (24°, 743.5 mm.) at 560°. The length of the furnace was 30 cm., the effective volume of the reaction tube was 77 cc., and the duration of the run was thirty-three minutes. Some liquid products were formed. There was 3720 cc. of exit gas which contained 61.6% of 1-butyne; hence, the extent of decomposition was 54%. The gas was analyzed by absorbing the 1-butyne with potassium iodomercurate solution, and the unabsorbed gas was passed through a small pipet containing molten maleic anhydride. This reagent absorbs 1,3-butadiene quantitatively,[10] but no gas was ab-

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(8) Hurd and Christ, THIS JOURNAL, **57**, 2007 (1935).

(9) Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

(10) Tropsch and Mattox, *Ind. Eng. Chem., Anal. Ed.*, **6**, 104 (1934); Korotkov, *Sintet. Kauchuk*, No. 4, 29–31 (1933); *C. A.*, **28**, 3028 (1934).

sorbed. The percentage of gas which dissolved in 82.5% sulfuric acid was 2.1. Methylallene should make up much of this portion. The remainder was discarded.

Summary

1-Hexyne and 1-heptyne were pyrolyzed at temperatures of 500, 550 and 600°. The chief gaseous products were propylene, methane and ethylene but some ethane and hydrogen were formed also. By ozonolysis it was established that the liquid products from 1-hexyne contained 1,2-hexadiene, and that the liquids from 1-heptyne contained 1,2-heptadiene. Except in the experiment at 600°, there was no evidence for the production of 2-alkynes, and then only in traces. Aromatic hydrocarbons or 1,3-alkadienes were not formed. Similarly, in work with 1-butyne at 560°, the absence of 1,3-butadiene was established. The rearrangement of 1-alkynes into 1,2-alkadienes does not proceed at 400°, but requires temperatures which are high enough to cause concurrent breakdown into gaseous products. The significance of this fact is brought out in the reaction mechanism.

EVANSTON, ILLINOIS RECEIVED JULY 6, 1937

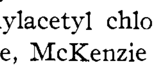
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Action of Aluminum Chloride on Phenyl-α-naphthylacetyl Chloride[1]

BY C. F. KOELSCH AND H. J. RICHTER

Diphenylacetyl chloride in the presence of aluminum chloride reacts with benzene to give diphenylacetophenone[2] and with naphthalene to give diphenylacetonaphthalene.[3] In attempting to carry out an analogous reaction with phenyl-α-naphthylacetyl chloride, aluminum chloride and benzene, McKenzie and Tattersall[4] obtained not the expected phenyl-α-naphthylacetophenone, but rather a compound, $C_{18}H_{12}O$, formed by the abstraction of hydrogen chloride from the acid chloride. Further than noting that this product did not have the properties of a ketene, these investigators made no suggestions as to its possible structure.

Since α-naphthylacetyl chloride has been shown to yield acenaphthenone on treatment with aluminum chloride in nitrobenzene,[5] it appeared possible that McKenzie and Tattersall's compound was an acenaphthenone derivative. We have found that oxidation of McKenzie and Tattersall's compound yields 8-benzoylnaphthoic acid, indicating that it is to be formulated as 7-phenylacenaphthenone (I) or the enol of this.



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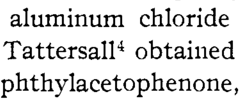

II

The ketonic formula best represents the behavior of the substance. It is not attacked by bromine, even in boiling acetic acid; it is colorless, while all acenaphthylene derivatives are colored; and, finally, it reacts with phenylmagnesium bromide to give an oily addition product which yields the known orange diphenylacenaphthylene (II) on dehydration. The compound may react in the enolic form, however, for when its solution in pyridine is treated with benzoyl chloride it gives an orange benzoate, whose color indicates that it is an O- rather than a C-derivative. The red color developed when alkali is added to an alcohol solution of the ketone also indicates enolization, but no methyl derivative could be obtained when such a solution was treated alternately with sodium hydroxide and methyl sulfate.

Experimental

7-Phenylacenaphthenone (I).—The following procedure was found to give a considerably better yield than that of McKenzie and Tattersall. A solution of phenyl-α-naphthylacetic acid (25 g.) in 250 ml. of benzene was treated with 20 g. of phosphorus pentachloride and boiled until hydrogen chloride was no longer evolved. Aluminum chloride (14 g.) was then added in portions, the mixture refluxed for one hour, and decomposed with iced hydrochloric acid. The oil left after the benzene had been steam distilled was distilled under reduced pressure, yielding 16 g. of an oil which rapidly solidified. The crude product melted at 106–111°, and, when purified, at 115.5–116.5° in agreement with the reported value.

Oxidation.—A solution of 2 g. of the ketone in 15 ml. of acetic acid was treated with 2 g. of chromic acid, kept at 80° for thirty minutes, and poured into water. From the precipitated organic substances taken up in ether, sodium

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(1) Abstracted from the thesis of H. J. Richter submitted to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the M.S. degree, October, 1935.

(2) Klingeman, *Ann.*, **275**, 83 (1893).

(3) McKenzie and Dennler, *J. Chem. Soc.*, **125**, 2105 (1924).

(4) McKenzie and Tattersall, *ibid.*, **127**, 2522 (1925).

(5) German Patent 230,237, *Chem. Centr.*, **82**, I, 359 (1911).