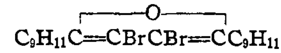
concd. nitric acid. It crystallized from ethanol and melted at 107.5–108° (corr.).

Anal. Calcd. for $C_{22}H_{23}O_3N$: C, 74.7; H, 6.5; N, 4.0. Found: C, 75.3; H, 6.5; N, 4.1.



$C_9H_{11}C{=}CBrCBr{=}CC_9H_{11}$ (O bridging the two terminal C), **2,5-Dimesityl-3,4-dibromofuran.**—Attempts at direct bromination of the dimethylfuran gave oils. Only when the amount of bromine added was limited to two molecules was a crystalline product obtained. This proved to be the dibromo compound. It was best obtained by stepwise addition of bromine to a carbon tetrachloride solution of the furan. It was crystallized from ethyl acetate, acetone, and ether–butanone mixtures, and melted at 146.5–147°.

Anal. Calcd. for $C_{22}H_{22}OBr_2$: C, 57.14; H, 4.8. Found: C, 57.45; H, 4.9.

When bromination of IV or VIII was carried out in carbon disulfide with ferric bromide as catalyst, a product was obtained which appeared to be a pentabromo compound. This is being investigated further.

The reaction between phosphorus pentabromide and di-(trimethylbenzoyl)-ethylene gave di-(trimethylbenzoyl)-dibromoethane. From I only intractable products were obtained.

1,2-Di-(3-bromo-2,4,6-trimethylbenzoyl)-ethylene, VI.—Ten grams of fumaryl chloride, V, was added slowly to a well-stirred mixture of 150 cc. of carbon disulfide, 30 cc. of bromomesitylene, and 60 g. of aluminum chloride, the mixture being allowed to stand with stirring for forty-five minutes and decomposed in ice in the usual way. The product was obtained in a yield of 50%; it was crystallized from chloroform and ethyl acetate; m. p. 228–230° (pale yellow).

Anal. Calcd. for $C_{22}H_{22}O_2Br_2$: C, 55.2; H, 4.6; Br, 33.4. Found: C, 55.0; H, 4.9; Br, 33.8.

1,2-Di-(3-bromo-2,4,6-trimethylbenzoyl)-ethane, VII, was prepared by adding an excess of zinc dust to a boiling solution of 3 g. of VI in 150 cc. of glacial acetic acid, allowing the mixture to boil gently for one minute and filtering and washing the zinc residue with more hot acetic acid. On diluting with a little water and cooling, 3 g. of nearly pure VII separated and was recrystallized from ethyl acetate; m. p. 183–184°.

Anal. Calcd. for $C_{22}H_{24}O_2Br_2$: C, 55.0; H, 4.5. Found: C, 55.0; H, 5.3.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-furan, VIII.—Attempts to dehydrate VII with acetic anhydride and sulfuric acid failed, also heating with mixtures of concd. hydriodic acid and concd. acetic acid.

Half a gram of VII with 1.5 cc. of hydriodic acid (sp. gr. 1.7) was sealed in a tube and heated at 182–185° for one hour. The tube was cooled in ice, opened, and the hydriodic acid decanted from the resinous product which was washed with cold water and digested with methanol, the furan crystallizing. It was recrystallized from ethanol–ethyl acetate mixtures and melted at 92–94°.

Anal. Calcd. for $C_{22}H_{22}OBr_2$: C, 57.1; H, 4.8. Found: C, 57.3; H, 4.9.

Summary

The preparations of 2,5-dimesityl- and 2,5-di-(bromomesityl)-furans are described and the effect of the mesityl groups on the ease of furan ring closure is discussed.

CHARLOTTESVILLE, VA. RECEIVED JANUARY 18, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Catalytic Hydration of Alkylacetylenes[1]

BY ROBERT J. THOMAS, KENNETH N. CAMPBELL AND G. F. HENNION

Introduction

Surprisingly little work has been reported in the literature concerning the hydration of alkylacetylenes to ketones.

$$R{-}C{\equiv}CH + HOH \longrightarrow R{-}CO{-}CH_3$$

Propyne,[2] 1-pentyne,[3] 2-hexyne,[4,5] 1-heptyne,[6] 3-heptyne,[7] 1-octyne[6,8] and 2-octyne[7] have been converted to their corresponding ketones by the action of strong sulfuric acid. The yields obtained by this method are low because of polymerization and charring. Desgrez[9] was able to obtain ketones from several alkylacetylenes by heating them with water in sealed tubes at high temperatures. In this case also the yields were low.

Kutscheroff[10] succeeded in hydrating propyne to acetone under mild conditions by the use of dilute sulfuric acid and mercuric salts as catalysts. As is well known this method finds commercial application in the production of acetaldehyde from acetylene. Carter[11] and Conaway[12]

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[1] Paper XXIV on the chemistry of the alkylacetylenes and their addition compounds; previous paper, THIS JOURNAL, **60**, 568 (1938).

[2] Schrohe, *Ber.*, **8**, 367 (1875).

[3] Faworski, *J. prakt. Chem.*, [2] **37**, 388 (1888).

[4] Faworski, *ibid.*, [2] **37**, 428 (1888).

[5] Michael, *Ber.*, **39**, 2147 (1906).

[6] Béhal, *Ann. chim.*, [6] **15**, 267 (1888).

[7] Béhal, *ibid.*, [6] **15**, 408 (1888).

[8] Béhal, *Bull. soc. chim.*, [2] **47**, 33 (1887).

[9] Desgrez, *Ann. chim.*, [7] **3**, 209 (1894).

[10] Kutscheroff, *Ber.*, **17**, 13 (1884).

[11] Carter, U. S. Patent 1,896,161 (1933); *C. A.*, **27**, 2458 (1933).

[12] Conaway, U. S. Patent 1,967,225 (1934); *C. A.*, **28**, 5834 (1934).

also have used it to obtain methyl vinyl ketone from vinylacetylene. The catalytic method has not been applied previously to the hydration of higher alkylacetylenes.

In the hydration of acetylene, propyne and vinylacetylene, water solutions of the catalyst are entirely satisfactory because the product is, in each case, water soluble. Furthermore, these acetylenes are gases and they may be introduced at such a rate that the reacting medium is homogeneous at all times. In the case of the higher acetylenes, however, neither the acetylene nor the ketone produced is water soluble. Consequently it was of interest to investigate the catalytic hydration of higher acetylenes in solvent combinations which would maintain the respective products in solution and thus favor smooth reactions and high yields. 1-Hexyne, 1-heptyne and 1-octyne were selected for these studies.

Preliminary to the investigation, the solubilities of 1-hexyne and 2-hexanone in various aqueous solvents were determined on a quantitative basis. The solubility relationships were found to be excellent in a number of instances and the matter was not further investigated. A summarized account of the data is presented in Tables I and II.

TABLE I

SOLUBILITIES OF 1-HEXYNE IN AQUEOUS SOLVENTS

Solvent	Grams of solvent per mole of 1-hexyne, at 40°	50°	60°	70°
70% methanol	692	582	470	363
80% acetic acid	...	437	365	300
80% acetone	436	405	372	335

TABLE II

SOLUBILITIES OF 2-HEXANONE IN AQUEOUS SOLVENTS

Solvent	Grams of solvent per mole of 2-hexanone, at 40°	50°	60°	70°
40% methanol	605	490	386	306
60% acetone	401	388	373	355
70% acetone	248	238	228	217
50% acetic acid	209	198	185	170
50% methanol	133	116	100	87
60% acetic acid	94	86	76	65

With the help of the above data the hydration of 1-hexyne, 1-heptyne and 1-octyne in aqueous solvents was carried out, using as catalysts small amounts of mercuric sulfate and sulfuric acid.

Experimental

Hydration of 1-Hexyne.—One gram of mercuric sulfate, 1 g. of sulfuric acid and a suitable amount of solvent (150 g. of 70% methanol, 150 g. of 70% acetone, or 50 g. of 60% acetic acid) were placed in a 500-cc. 3-necked flask equipped with a mercury-sealed stirrer, reflux condenser and dropping funnel. The mixture was kept at 60 (±1°) and 0.5 mole (41.0 g.) of 1-hexyne[13] was added, with good stirring, over a period of one hour. The reaction mixture was then stirred at 60° for an additional three hours and cooled to room temperature.

When the solvent used was methanol or acetone a considerable portion of it was removed by fractional distillation through an efficient double-jacketed column (120 cm. × 5 mm.) packed with a single monel wire spiral. The residue was saturated with solid sodium chloride and the two layers separated. The organic layer was washed with sodium chloride solution, then with sodium carbonate solution and again with salt solution. It was dried over calcium chloride and was then distilled from a modified Claisen flask. The portion of the distillate boiling between 124 and 128° was retained as 2-hexanone.

When 60% acetic acid was used as the solvent the procedure was modified as follows. The solvent was not removed by distillation. Instead, the cooled reaction mixture was treated with a solution of 28 g. of sodium carbonate in 75 ml. of water to neutralize all acid. The mixture was saturated with sodium chloride, the organic layer separated and worked up as described above.

Hydration of 1-Heptyne and 1-Octyne.—These acetylenes[13] were hydrated in aqueous acetic acid as described above for 1-hexyne. A reaction temperature of 70° was found suitable for 1-heptyne and 80° for 1-octyne.

The results of the various experiments are tabulated in Table III. The physical properties of the three ketones prepared are given in Table IV.

TABLE III

EXPERIMENTAL DATA, HYDRATION OF 0.5 MOLE RUNS OF ALKYLACETYLENES

Acetylene	Solvent Nature	Solvent Wt., g.	$HgSO_4$, g.	H_2SO_4, g.	Temp., °C.	Ketone, % yield
1-Hexyne	70% methanol	150	1	1	60	79.8
1-Hexyne	70% acetone	150	1	1	60[a]	63.6
1-Hexyne	70% acetone	150	5	5	60[a]	78.4
1-Hexyne	60% acetic acid	50	1	0	60[a]	38.6
1-Hexyne	60% acetic acid	50	1	1	60[b]	78.6
1-Heptyne	60% acetic acid	50	1	1	70[b]	87.1
1-Octyne	65% acetic acid	50	1	1	80[b]	91.2

[a] Appreciable amount of insoluble liquid phase after three hours. [b] Liquid phase not entirely homogeneous after three hours.

TABLE IV

PROPERTIES OF KETONES PREPARED

Ketone	B. p., °C.	$n^{25}D$	d^{25}
2-Hexanone	127	1.3985	0.8077
2-Heptanone	148–149	1.4066	.8135
2-Octanone	169–170	1.4134	.8181

Discussion

It will be noted from Table I that 235 g. of 70% methanol is required to dissolve 0.5 mole of 1-hexyne at 60°, while 2-hexanone is extremely soluble in this solvent. It was found, however, that hydration of 1-hexyne proceeded rapidly enough so that the solution remained practically

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[13] Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

homogeneous when only 150 g. of the solvent was used. When 70% acetone was used as a solvent hydration did not take place rapidly enough to maintain miscibility, although more solvent was used than was required to keep the 2-hexanone in solution.

When hydration of 1-hexyne was carried out in 60% acetic acid it proceeded sufficiently rapidly so that the mixture remained practically homogeneous despite the fact that much less solvent was used than required to dissolve the acetylene.

In the cases of hydration with aqueous methanol or acetic acid it is possible that the organic solvent may react with the acetylene by addition.[14,15] The resulting ketal or ester would hydrolyze to ketone under the conditions of the experiments.

A number of experiments were performed with the object of determining the mechanical losses which resulted from washing, drying and distilling the products. These were found to amount to 10–15% of the material when half-mole quantities of the acetylenes were used. Consequently the actual extent of hydration was, in each case, considerably higher than indicated in Table III.

The application of this method to the hydration of other acetylenic compounds is being further studied in this Laboratory.

Summary

Catalytic hydration of three higher alkylacetylenes to ketones has been accomplished readily and with excellent yields by use of aqueous solvents.

NOTRE DAME, INDIANA RECEIVED NOVEMBER 29, 1937

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[14] Killian, Hennion and Nieuwland, THIS JOURNAL, **56**, 1384 (1934).

[15] Hennion and Nieuwland, *ibid.*, **56**, 1802 (1934).

NOTES

The Explosion of Chloroform with Alkali Metals

BY TENNEY L. DAVIS AND JOHN O. MCLEAN

The explosion which occurs when chloroform and sodium in contact with each other are subjected to shock seems to have been discussed for the first time in 1925 by Staudinger,[1] who described a safe technique for demonstrating it and reported only sodium chloride and carbon as the products. We have wished to account for the hydrogen which the chloroform contains and to identify other products in the hope that light might be thrown upon the mechanism of the reaction.

About 0.3 g. of sodium or of potassium or of the liquid alloy was sealed up in a small glass bulb, 6 to 8 mm. in diameter, which had a capillary stem 15 to 20 mm. in length. This was placed in the bottom of a narrow test-tube and held in place by a collar of glass (a section of glass tubing) which was sintered to the inner wall of the test-tube. The latter was then drawn down, chloroform (1 to 2 cc.) was introduced, and the explosive capsule was sealed. These capsules could be prepared in advance and could be kept safely as long as desired.

For studying the products of the explosion a steel bomb, such as is used for laboratory high pressure syntheses, was taken, about 25 cm. long and having a capacity of 380 cc. It was equipped with valves and copper tubes, by means of which the bomb was flushed out with nitrogen for at least fifteen minutes before each experiment, the pressure existing in the bomb after the explosion was determined, and the gaseous products were swept out with nitrogen. The inside of the bomb was fitted with a cylindrical block of steel by which the explosive capsule was gripped and by the crushing action of which it was fired. The details of the apparatus are shown in Fig. 1. The steel block and capsule being at the end of the bomb which is uppermost in the figure, the explosion was made to occur by inverting the bomb quickly or by dropping it on the floor. The explosion produced heat enough to make the bomb perceptibly warm to the touch.

When one of the capsules was dropped on the concrete pavement from a height of 2 meters, a loud explosion was produced, accompanied by a flash which was visible even in the sunlight, and a cloud of white smoke or mist which smelled distinctly of phosgene.

When the explosion occurred in the bomb in an atmosphere of nitrogen, the interior of the bomb was found to be covered with a deposit of soot. After the bomb had resumed room temperature, the pressure within it was determined by means of a manometer, and the gases were swept out by a stream of nitrogen and bubbled through water for the removal of hydrogen chloride, until a total of 1800 cc. of the mixed gases (mostly nitrogen) had been collected. Twenty-five cc. portions ($^1/_{72}$ of the whole)

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[1] Staudinger, *Z. Elektrochem.*, **31**, 549 (1925).