TABLE III

SUBSTITUTED DI-PHENYLETHYNYL MERCURYS

Phenyl-acetylene	Formula	M. p., °C.	Mercury, % Calcd.	Mercury, % Found
.....	$(C_6H_5C{\equiv}C)_2Hg$	124.5–125[b]	...	...
p-Methyl	$(CH_3C_6H_4C{\equiv}C)_2Hg$	199–202[b]	...	...
p-Ethyl[a]	$(C_2H_5C_6H_4C{\equiv}C)_2Hg$	142–143	43.51	44.02
p-Isopropyl[a]	$(C_3H_7C_6H_4C{\equiv}C)_2Hg$	109–110	41.21	40.95
p-Chloro[a]	$(ClC_6H_4C{\equiv}C)_2Hg$	221–222	42.54	42.56
m-Chloro[a]	$(ClC_6H_4C{\equiv}C)_2Hg$	138–139	42.54	42.85
o-Chloro[a]	$(ClC_6H_4C{\equiv}C)_2Hg$	213–214	42.54	42.66
p-Bromo[a]	$(BrC_6H_4C{\equiv}C)_2Hg$	256–257	35.79	35.88
m-Bromo[a]	$(BrC_6H_4C{\equiv}C)_2Hg$	143–144	35.79	35.97
o-Bromo[a]	$(BrC_6H_4C{\equiv}C)_2Hg$	184–185	35.79	35.61

[a] New compound. [b] Johnson and McEwen, Ref. 6.

Summary

1. Four new substituted phenylacetylenes and three new phenylpropiolic acids have been described.

2. Eight mercury derivatives of substituted phenylacetylenes have been prepared, described and analyzed.

3. The properties of *p*-ethyl- and *p*-isopropylphenylacetylene have been reported.

NOTRE DAME, INDIANA RECEIVED APRIL 2, 1934

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Hydrolysis of Tertiary Aliphatic Halides. I

BY H. MILTON WOODBURN AND F. C. WHITMORE

Our attention was drawn to this subject by difficulties which we experienced in attempting to prepare tertiary amyl alcohol by the hydrolysis of its chloride. We were further interested in this process by statements made by Ayres regarding the hydrolysis of amyl chlorides.[1] A study of the literature revealed considerable confusion on the subject.[2] In the present work experiments were conducted with tertiary butyl chloride, tertiary amyl chloride and bromide, methyldibutylcarbinyl chloride[3] and tri-*n*-butylcarbinyl chloride.[3] The results of these experiments gave definite results which can be summarized in the following statements.

1. The ease of hydrolysis of a tertiary chloride with hot water or sodium carbonate solution decreases with increasing molecular weight, probably because of decreasing solubility. Comparable experiments with tertiary butyl chloride and tributylcarbinyl chloride with hot water gave 5.7 and 0.05 g. of hydrochloric acid liberated, respectively.

2. The hydrolysis of tertiary chlorides is dependent on their solubility in the hydrolyzing medium. Thus the rate of hydrolysis of tertiary butyl and tertiary amyl chlorides is greater in pure water than in 5% sodium carbonate solution. The rate is still slower with 40% sodium carbonate solution.

3. The hydrolysis of tertiary chlorides with hot water or sodium carbonate solution gives olefins exclusively. With *cold* water or *cold* sodium hydroxide solution, a certain amount of tertiary alcohol is formed along with the olefin.

4. Tertiary halides are more resistant to hydrolysis than is ordinarily supposed.

Experimental

Preparation of the Halides.—Tertiary butyl chloride and tertiary amyl chloride were prepared by the method of Norris.[4] Tertiary amyl bromide was best made by the action of hydrogen bromide gas with trimethylethylene prepared by dehydrating commercial tertiary amyl alcohol[5] with 15% sulfuric acid. The product boiled at 44–47° (80 mm.). The higher tertiary chlorides were available from another research.[3]

Hydrolysis Experiments.—Measured amounts of the halides and water or the aqueous reagents were stirred mechanically in the cold or at the refluxing temperature or were merely refluxed.

The liberated inorganic halide (halogen acid or sodium halide) was determined by titration with standard silver nitrate (0.1058 *N*) and potassium thiocyanate (0.1178 *N*) according to Volhard.

The results of the experiments are summarized in Table I.

TABLE I

Tertiary halide	Cc.	Reagent	Cc.	Conditions	Time, min.	Halogen reacted, %
BuCl	25	Water	50	Shake, cold	2	1.2
BuCl	25	Water	50	Reflux	480	71.0
BuCl	25	5% Na_2CO_3	50	Reflux	480	43.4
AmCl	50	Water	100	Shake, cold	2	0.3
AmCl	50	Water	100	Reflux	540	48.6
AmCl	50	5% Na_2CO_3	100	Reflux	540	44.5
AmCl	50	40% Na_2CO_3	100	Reflux	1020	20.0
AmCl	50	2% H_2SO_4	100	Reflux	540	46.8

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(1) Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929).

(2) Butlerow, *Ann.*, **144**, 6, 33 (1867); Straus, *ibid.*, **370**, 366 (1909); Michael and Leupold, *ibid.*, **379**, 287 (1911); Dobbin, *J. Chem. Soc.*, **37**, 237 (1880); Bauer, *Ann.*, **220**, 158 (1889); Friedel and Silva, *Jahresb.*, 339 (1873); Wislicenus, *Ann.*, **219**, 319 (1889); Slawjanow, *Chem. Zentr.*, 11, 134 (1907); Mereshkowski, *ibid.*, 1, 1814 (1914); Muset, *ibid.*, 1, 1313 (1907).

(3) Whitmore and Woodburn, THIS JOURNAL, **55**, 361 (1933).

(4) Norris, "Organic Syntheses," 1928, Vol. V111, p. 50.

(5) Supplied by the Sharples Solvents Corp., Philadelphia, Pa.

TABLE I (*Concluded*)

Tertiary halide	Cc.	Reagent	Cc.	Conditions	Time, min.	Halogen reacted, %
AmCl	50	5% Na_2CO_3	100	Reflux, stir[a]	480	81.1
AmCl	50	Water	100	Reflux, stir	450	81.8
AmCl	125[b]	Water	125	Stir, cold	540	54.8[c]
		Water	125	Stir, cold	240	24.2
		Water	100	Stir, cold	870	15.4
		Water	100	Stir, cold	420	1.2
		Water	100	Stir, cold	180	0.1
				Total	2250	95.7[d,e]
AmCl	125[f]	1.4 *N* NaOH	125	Stir, cold	540	60.0
		1.4 *N* NaOH	125	Stir, cold	240	23.9
			100	Stir, cold	870	14.8
			100	Stir, cold	420	2.8
				Total	2070	100.5[g]
AmBr	57 g.	Water	150	Reflux,[h] stir	270	87.0[i]
AmBr	57 g.	Water	150	Cold, stir	270	46.5[j]
$MeBu_2CCl$	15 g.	Water	35	Reflux	450	14.0
Bu_3CCl	25 g.	Water	100	Reflux	480	1.2
	25 g.	5% Na_2CO_3	100	Reflux	480	1.3

[a] Vigorous mechanical stirring during the refluxing.
[b] In this experiment the organic layer was separated and shaken with a fresh portion of water. This was continued until practically no acid was removed by this treatment.
[c] This and the other figures in this experiment were obtained by titration with standard alkali.
[d] A Volhard titration of an aliquot part of the combined water layers gave 92%.
[e] The combined aqueous layers were fractionated through a 60 × 1.5 cm. packed adiabatic column using a high reflux ratio. The organic layer was similarly fractionated. The result was the isolation of 17.3 g. of trimethylethylene and 8.4 g. of tertiary amyl alcohol (b. p. 100–101°, n^{20}_{D} 1.4050).
[f] This was similar to the preceding experiment except that successive batches of standard alkali were used instead of pure water.
[g] Fractionation according to *e* gave 12 g. of trimethylethylene and 17.7 g. of tertiary amyl alcohol (b. p. 100–100.6°, n^{20}_{D} 1.4035).
[h] The reflux condenser was kept at 40° to allow the trimethylethylene to pass over to a cold condenser as fast as formed. The yield of olefin was 80%.
[i] The trimethylethylene boiled at 37–38.5°. Only 1.5 g. of higher boiling material was obtained.
[j] The ratio of olefin to carbinol was 1:2.

Summary

1. Experiments have been conducted on the hydrolysis of several tertiary aliphatic halides under various conditions.

STATE COLLEGE, PENNA.

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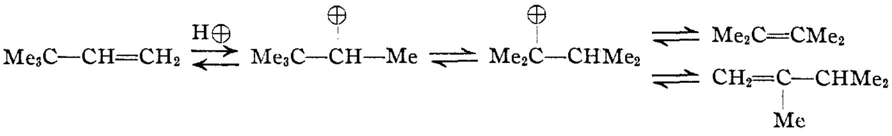
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Isomerization of Olefins. I. Conversion of *t*-Butylethylene, *unsym*-Methylisopropylethylene and Tetramethylethylene to Equilibrium Mixtures of the Three Olefins[1]

BY K. C. LAUGHLIN, C. W. NASH AND FRANK C. WHITMORE

When the dehydration of an alcohol gives more than one olefin, these may be formed directly by the action of the dehydrating agent with the alcohol or one olefin may be formed from another by an isomerizing action of the dehydrating agent. While it has long been known that such "contact isomerization" can shift the position of a double bond in a given carbon skeleton,[1a] it has remained for the present study to prove that this process can also involve the rearrangement of an alkyl group to give a new carbon skeleton.

The dehydration of methyl-*t*-butylcarbinol (pinacolyl alcohol)[2] by a catalyst consisting of phosphorus pentoxide on silica gel in a flow reactor at 300° has been found to give tetramethylethylene, *unsym*-methylisopropylethylene and *t*-butylethylene in the ratio 61:31:3. When each of these olefins was prepared pure and passed over the same catalyst under the same conditions, it gave a mixture of essentially the same composition as that obtained from the alcohol. The interconversion of the olefins probably takes place through the addition of a proton from the catalyst to one olefinic carbon, leaving the other carbon with only six electrons and thus inducing the usual rearrangements.[3] The changes involved may be the following



$$Me_3C{-}CH{=}CH_2 \underset{}{\overset{H\oplus}{\rightleftharpoons}} Me_3C{-}\overset{\oplus}{C}H{-}Me \rightleftharpoons Me_2\overset{\oplus}{C}{-}CHMe_2 \begin{array}{l} \rightleftharpoons Me_2C{=}CMe_2 \\ \rightleftharpoons CH_2{=}\underset{Me}{\underset{|}{C}}{-}CHMe_2 \end{array}$$

These results show that the formation of a given olefin from an alcohol must not be assumed to be a simple or direct process.

Experimental

The dehydration of dimethylisopropylcarbinol is the best source of *unsym*-methylisopropylethylene. The carbinol was prepared in 41% yield from isopropylmagnesium bromide and acetone. It formed an azeotropic mixture with mesityl oxide formed by the condensing action of the Grig-

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(1) Original manuscript received October 2, 1933.

(1a) Ipatief, *Ber.*, **36**, 2003 (1903).

(2) Whitmore and Meunier, THIS JOURNAL, **55**, 3721 (1933).

(3) Whitmore, *ibid.*, **54**, 3274 (1932).