

TABLE III  
EFFECT OF PALLADIUM ON THE DECOMPOSITION OF *t*-  
BUTYL HYDROPEROXIDE

Time, min.	0	10	23	52
0.01982 <i>N</i> thio, cc.	66.0	38.0	22.0	21.7

The results in Table III seem to indicate that palladium black slowly accelerates the decomposition of *t*-butyl hydroperoxide in a dilute solution of disodium phosphate. However, pure *t*-butyl hydroperoxide is only slowly attacked by palladium black and a pure sample of it stirred over this catalyst for several months was still strongly peroxidic.

### Summary

1. *t*-Butyl hydroperoxide has been prepared

by the fractionation of an anhydrous solution of hydrogen peroxide in *t*-butyl alcohol in the presence of dehydrating agents.

2. This peroxide has been found to be very stable under ordinary conditions.

3. Pure liver catalase and horse-radish peroxidase have very little or no effect on the decomposition of *t*-butyl hydroperoxide.

4. Palladium black catalyzes slowly the decomposition of *t*-butyl hydroperoxide in dilute solution of disodium phosphate, although the decomposition of the peroxide is only slightly affected by this catalyst.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

## Lengthening Carbon Chains by Three Units: Assay of Primary Bromides from the Addition of Hydrogen Bromide

BY A. P. KOZACIK AND E. EMMET REID

It is well known that an alkyl bromide may be converted into a primary alcohol with either one or two additional carbon atoms in the chain. The object of this investigation was to provide a method of lengthening a carbon chain by three  $-\text{CH}_2-$  units:  $\text{RBr} \rightarrow \text{RMgBr} \rightarrow \text{RCH}_2\text{CH}=\text{CH}_2 \rightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{Br}$ . This combines an old reaction with one<sup>1</sup> that has been studied only recently. In addition to lengthening the chain this gives odd-numbered bromides from the readily obtainable even. It was particularly interesting to extend these reactions to the higher alkyls and to aromatics. Another object was to identify the primary bromides by crystalline derivatives and to get a rough estimate of their purity. The abnormal addition of hydrogen bromide is of great theoretical interest; the availability of the primary bromides so produced for syntheses is

a practical question of importance. The alkenes are given in Table I.

The addition of the hydrogen bromide was carried out by Professor Kharasch.<sup>2</sup> Our results show conclusively that the primary bromides are obtained. The melting points of these are in Table II. It was too much to expect that the technique which he has developed for the lower alkenes would apply to the higher without some modification. Unfortunately the whole amounts of the alkenes that were available were run through with the standard technique before any of the products were tested. The results were good with nonene-1 but very poor for heptadecene-1 and nonadecene-1. The identity of the synthetic bromides was shown and their approximate purity estimated by their reaction with para substituted phenols. For compari-

TABLE I  
PROPERTIES OF THE ALKENES

Alkenes	B. p., °C.	Press., mm.	M. p., °C.	$d_4^{20}$	$d_4^{25}$	$n_D^{20}$	Bromine no.			Yield, %
							Calcd.	Found	Found	
$n\text{-C}_{11}\text{H}_{23}\text{CH}=\text{CH}_2$	102-103	10	-13	0.7856	0.7670	1.4328	62.8	63.6	63.7	77
$n\text{-C}_{13}\text{H}_{27}\text{CH}=\text{CH}_2$	127.5-128.5	10	-2.8	.7921	.7751	1.4353	55.7	54.5	54.6	67
$n\text{-C}_{15}\text{H}_{31}\text{CH}=\text{CH}_2$	155.4-156.4	10	11.2	.7892 <sup>20</sup>	.7859	1.4417	49.7	47.7	48.5	43
$n\text{-C}_{17}\text{H}_{35}\text{CH}=\text{CH}_2$	177	10	21.7	.7889 <sup>20</sup>	.7858 <sup>24</sup>		46.9	45.7		56
$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CH}=\text{CH}_2$	181-182	757								77
$\text{C}_6\text{H}_5(\text{CH}_2)_3\text{CH}=\text{CH}_2$	94.5-95	10								87

(1) Kharasch and co-workers, THIS JOURNAL, **58**, 2469, 2521 and 2531 (1933).

(2) M. S. Kharasch and Wm. M. Potts, J. Org. Chem., **3**, 195 (1937).

son the authentic bromides previously prepared<sup>3</sup> were treated with the same phenols, under the same conditions and usually at the same time. The products were crystallized two or more times. The phenyl derivatives were treated with  $\beta$ -naphthol. Only in the case of 3-phenylpropyl bromide was an authentic sample available for comparison.

TABLE II  
MELTING POINTS OF AUTHENTIC (A) AND SYNTHETIC (S)  
BROMIDES AS RECEIVED

Carbons	A	S	Dif.	Minimum estimated purity
9				82
11	-13.15	-25	12	65
13	5.94	-15	21	41
15	18.63	7.4-8.4	10	60
17	28.40	1-2	26	12
19	38	13-15	23	3

From the results in Table III it will be seen that the products from the synthetic bromides are somewhat less in amount and melt lower than those from the authentic. The losses on the first crystallization are even more significant. Taking the data for the nonyl bromides, we find this loss to average 11% for the authentic and 28 for the synthetic. In the second crystallization the losses were nearly the same. For practical purposes the primary bromide present may be estimated by comparing the final yields of the twice crystallized derivatives with those from the authentic bromides. These estimates may be regarded as minimum values. Thus we can say that there was at least 82% of the primary bromide, and probably somewhat more, present in the synthetic nonyl bromide. The other syn-

TABLE III  
DERIVATIVES FROM AUTHENTIC AND SYNTHETIC BROMIDES  
AND *p*-SUBSTITUTED PHENOLS, *p*-XC<sub>6</sub>H<sub>4</sub>OH, YIELDS AND  
MELTING POINTS OF CRUDE AND CRYSTALLIZED

X		Yields, %		Loss on recrystallization, %		Melting points, °C.	
		A	S	A	S	A	S
From <i>n</i> -nonyl bromides							
C <sub>8</sub> H <sub>17</sub> O	Crude	87	81			58-59	
	1st cr.	78	60	10	26	58-59.5	54-55
	2nd cr.	73	56	6	7	60.0	60.0
C <sub>9</sub> H <sub>19</sub> O	Crude	85	84			62-63	57-59
	1st cr.	78	62	8	26	62.5-63	62-62.5
	2nd cr.	72	58	8	7	63.8	63.4
C <sub>11</sub> H <sub>23</sub> O	Crude	86	88			62-63.5	55-59
	1st cr.	76	61	12	31	64-64.5	63-64.5
	2nd cr.	..	57		7	65.2	64.8
C <sub>13</sub> H <sub>27</sub> O	Crude	86	86			64-66	60-63
	1st cr.	76	64	12	26	65-66	65-66
	2nd cr.	73	60	4	6	67.4	65-66

(3) Meyer and Reid, THIS JOURNAL, 58, 1577 (1933).

		From <i>n</i> -undecyl bromides					
C <sub>8</sub> H <sub>17</sub> O	Crude	99	67			59-60	52-56
	1st cr.	81	45	18	33	59-60	58-59
	2nd cr.	75	41	7	9	60.4	60.6
C <sub>10</sub> H <sub>21</sub> O	Crude	93	83			66-68	57-62
	1st cr.	76	51	18	38	68-69.5	67-68
	2nd cr.	71	46	7	10	69.8	69.8
C <sub>12</sub> H <sub>25</sub> O	Crude	76	73			66-69	58-63
	1st cr.	60	43	21	41	71-71.5	70-70.5
	2nd cr.	59	36	2	16	71.8	71.8
		From <i>n</i> -tridecyl bromides					
C <sub>8</sub> H <sub>9</sub> O	Crude	92	69			57-60	55-59
	1st cr.	82	29	11	58	61-62	60-61.5
	2nd cr.	70	27	15	7	62.8	62.8
C <sub>9</sub> H <sub>17</sub> O	Crude	95	67			62-63	55-60
	1st cr.	78	32	18	52	64-64.5	64-65
	2nd cr.	73	30	6	6	64.8	65.2
C <sub>10</sub> H <sub>21</sub> O	Crude	90	75			67-68	58-63
	1st cr.	79	25	12	67	67.5-68	67-67.5
	2nd cr.	72	23	8	8	67.6	67.5
		From <i>n</i> -pentadecyl bromides					
C <sub>11</sub> H <sub>23</sub> O	Crude	92	83			73-74	62
	1st cr.	73	54	21	35	74-75	72-74
	2nd cr.	67	40	8	26	75.6	74.2
Cl	Crude	95	71			44-47	39-44
	1st cr.	76	34	20	52	46-47	44-45.5
	2nd cr.	67	19	12	44	48.0	47.2
I	Crude	89	77			53-55	45-50
	1st cr.	66	37	27	52	56-57	55-56.5
	2nd cr.	57	33	12	11	57.2	57.0
		From <i>n</i> -heptadecyl bromides					
PhCH <sub>2</sub> O	Crude	89	67			88	80-84
	1st cr.	..	..			91.2	84-88
	2nd cr.	70	..			91.8	89.8
	3rd cr.	..	8				91.6
Cl	Crude	97	27			50-52	45
	1st cr.	86	3	11	89	53-54	52-53
	2nd cr.	81	..	6		54.2	53.8
I	Crude	96	44			60-61	57-59
	1st cr.	82	10	15	77	62-62.5	61-62
	2nd cr.	78	6	5	40	64.0	63.4
		From <i>n</i> -nonadecyl bromides					
H	Crude	98	8			51-55	47-51
	1st cr.	73	4	25	50	55-56	47-51
	2nd cr.	69	2	5	50	56.0	56.0

TABLE IV  
DERIVATIVES FROM AUTHENTIC AND SYNTHETIC PHENYL-  
ALKYL BROMIDES AND  $\beta$ -NAPHTHOL

	Yields, %	Loss on recrystallization		Melting points, °C.	
		A	S	A	S
From phenyl-propyl bromides					
Crude	63	59			66-67 62-64
1st cr.	47	44	25	25	69-69.5 68.5-69
2nd cr.	43	38	9	14	69.5-70 69.0-69.5
From phenyl-butyl bromide					
Crude	..	48			47-53
1st cr.	..	32		38	54-55
2nd cr.	..	26		19	54.5-55.5
From phenyl-hexyl bromide					
Crude	..	31			63-77
1st cr.	..	18		42	78-78.5
2nd cr.	..	15		17	78.5-79

thetic bromides do not show up so well: the undecyl may be estimated to contain at least 65% of the primary, the tridecyl, 41, the pentadecyl 60, the heptadecyl 12 and the nonadecyl only 3. The melting points of the bromides put them in the same order as to purity.

### Experimental

The procedure of Gilman<sup>4</sup> for the preparation of the Grignard reagents was followed. These reagents were used according to the method of Wilkinson,<sup>5</sup> for making the alkenes, which were separated from the disproportionation by-products of the Grignard reaction, heated with sodium and distilled. The properties of the new alkenes are to be found in Table I. The bromine numbers were determined by the method of Francis<sup>6</sup> as modified by Cortese.<sup>7</sup>

**Preparation of Derivatives.**—To prepare a derivative, 0.3 to 0.5 cc. of the alkyl halide was measured into a test-tube with 3 cc. of alcohol and about 10% excess of the phenol. As  $C_{19}H_{39}Br$  is a solid, it was weighed. This mixture was heated to effect solution and a slight excess of 1 *N* alcoholic potash added. The test-tube was stoppered loosely and placed with others in a beaker of water kept at about 70° for about twelve hours. At the end of the heating any alcohol that had evaporated was replaced and 2 cc. of hot water added. The mixture was boiled for a moment and then cooled quickly with violent shaking. This caused

the derivative to separate as a granular solid which was collected on a filter and washed twice with water. The product was crystallized twice or thrice from alcohol. For better comparison the derivatives of the authentic and synthetic bromides were prepared at the same time with the same reagents and the crystallizations were carried on side by side. The final melting points were kindly taken by Mrs. Carrie Gutman Moses with a standardized thermometer.

For preparing derivatives para substituted phenols were used. Experience in another investigation had shown that these give derivatives that are readily purified and melt at convenient temperatures. The monoalkyl hydroquinone ethers will be described later along with other derivatives made from them.

### Summary

1. A method has been devised for transforming an alkyl bromide into another alkyl bromide having a carbon chain longer by three units.
2. A method has been worked out for assaying the mixture of bromides obtained by the addition of hydrobromic acid to unsaturates.
3. By the preparation of known crystalline derivatives the formation of primary bromides by the addition of hydrobromic acid to alpha alkenes in the presence of peroxides has been confirmed.

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(4) Gilman, Zoellner and Dickey, *THIS JOURNAL*, **51**, 1579 (1929).(5) Wilkinson, *J. Chem. Soc.*, **120**, 3057 (1931).(6) Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).(7) Cortese, *Rec. trav. chim.*, **48**, 564 (1929).

(CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE)

## Sterols. XLIV. Pregnanone-3 and Related Compounds\*

BY RUSSELL E. MARKER AND ELMER J. LAWSON

Although all the pregnanediols, pregnanolones, and pregnanediones isomeric about  $C_3$ ,  $C_5$  and  $C_{20}$  have been described,<sup>1</sup> none of the corresponding pregnanols and pregnanones are known. Since we now have indications of the occurrence in urines of pregnane derivatives having only one oxygen atom,<sup>2</sup> we have begun the synthesis of compounds of this type for purposes of comparison and physiological testing. The present paper describes the preparation of pregnanone-3 and the isomeric 3-pregnanols.

Pregnanol-3( $\alpha$ )-one-20 was reduced by the Clemmensen method with amalgamated zinc and a mixture of acetic and concentrated hydrochloric acids. The reaction mixture, carried

through the acid succinate separation, yielded only 19 mg. of pregnanol-3( $\alpha$ ), but about 250 mg. (m. p. 102°) of what proved to be pregnanol-3 acetate could be crystallized from the non-hydroxylated fraction, and a further crop of pregnanol-3( $\alpha$ ) was obtained from the mother liquor after alkaline hydrolysis and acid succinate separation. The non-hydroxylated fraction, amounting to about 20% of the reaction mixture, did not yield any crystalline products.

Since it was thought at first that the crystalline product might be a pregnene, which could be identified by ozonolysis to give 3||4 pregnane-3,4-diacid,<sup>3</sup> or an isomer, this acid was prepared by the Clemmensen reduction of 20-keto-3||4-pregname-3,4-diacid.<sup>4</sup> The latter forms a 2,4-

(\*) Paper XLIII, *THIS JOURNAL*, **60**, 1904 (1938).(1) Marker, Kamm, Wittle, Oakwood, Lawson and Taucius, *THIS JOURNAL*, **59**, 2291 (1937).

(2) Unpublished results from This Laboratory.

(3) This nomenclature is suggested by Sobotka, "Chemistry of the Steroids," Williams and Wilkins, Baltimore, Md., 1938, p. 163.

(4) Butenandt, *Ber.*, **63**, 659 (1930); **64**, 2529 (1931).